Chemical phase and valence studies of plasma sprayed coatings: EDXRD and X-ray Absorption Spectroscopy (XAS) Results

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EDXRD (Energy Dispersive X-ray Diffraction) Facility/Program

Capabilities: 3D- Phase & strain mapping

Hardware: X17B1 National Synchrotron Light Source (ongoing)

Software: developed by Rutgers (freeware) (ongoing)

Mechanism for use: Rutgers contributing user NSLS X17B1

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L. Kabacoff Office of Naval Research

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Materials Plasma Spray ceramic coatings on metals

- μ-alumina-titania (87:13) coating [μ-AT]
- nano-alumina-titania (87:13)+ additives (ZrO_2 & CeO_2) coating [nATCZ]
- new TiO_2 coating

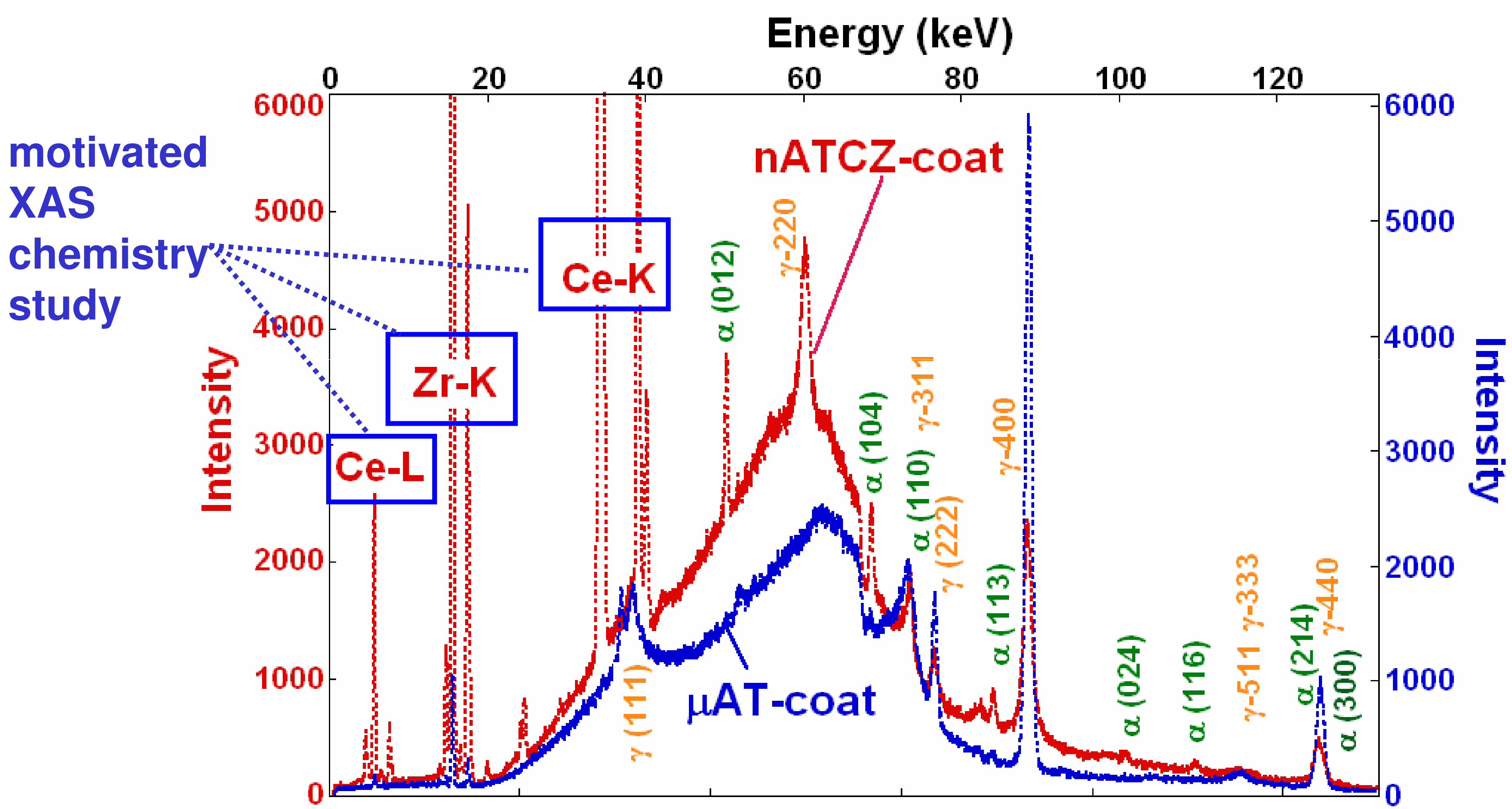
Characterization results

- **EDXRD** –structure
- X-ray Absorption Spectroscopy (XAS)
  - valence state-chemical effects
  - local ligand coordination
  - structure

EDXRD: plasma sprayed alumina-titania coatings (on Ti-6-4)

- nATCZ → nano composite alumina-titania coating (87:13) + additives ~ 8-10% ZrO_2 & 6-8 % CeO_2)

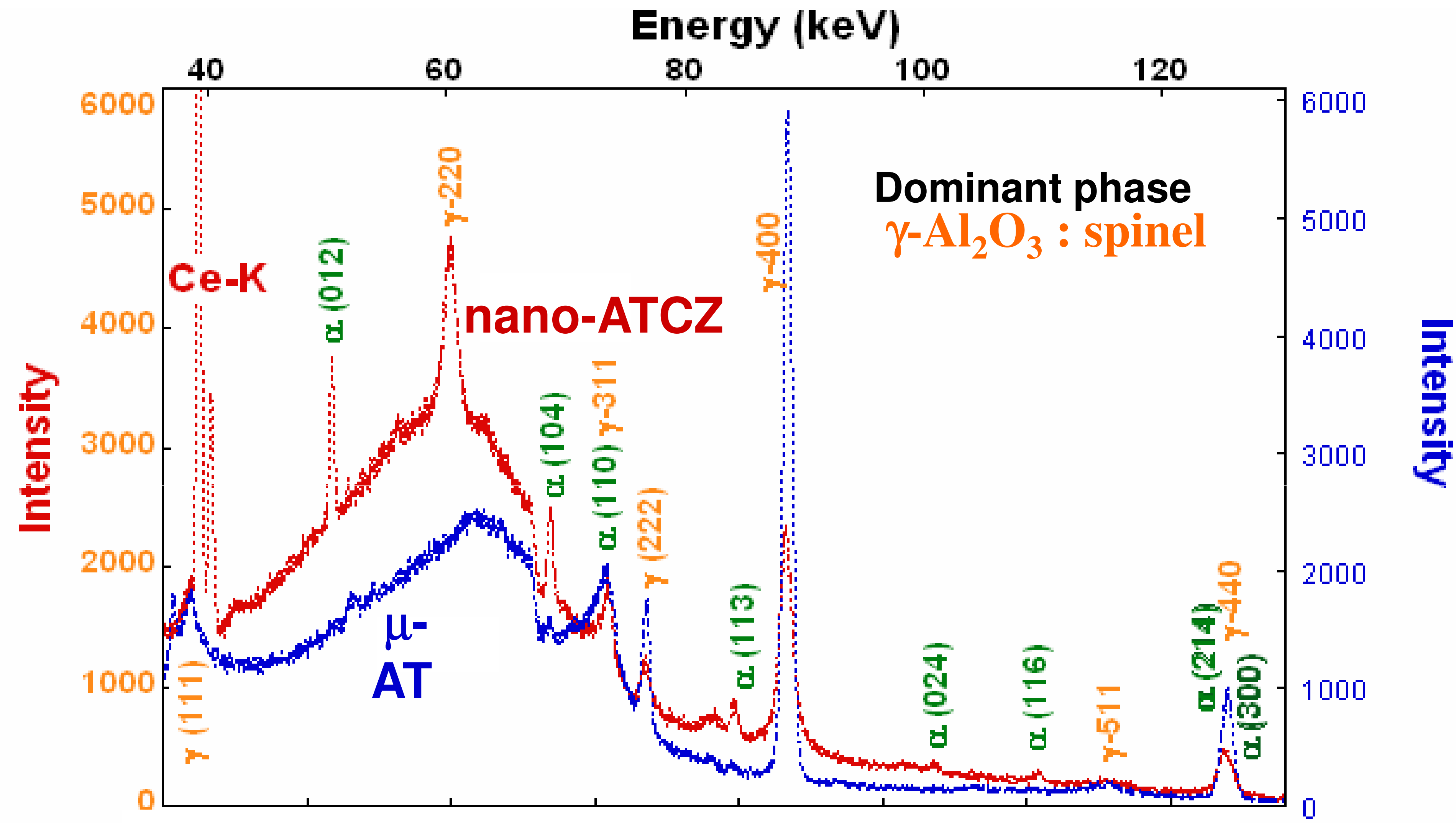
** %-ratios by weight



- μAT → micro-size alumina-titania (87:13) μAT coating

EDXRD –structure

Coatings: delaminated & powdered



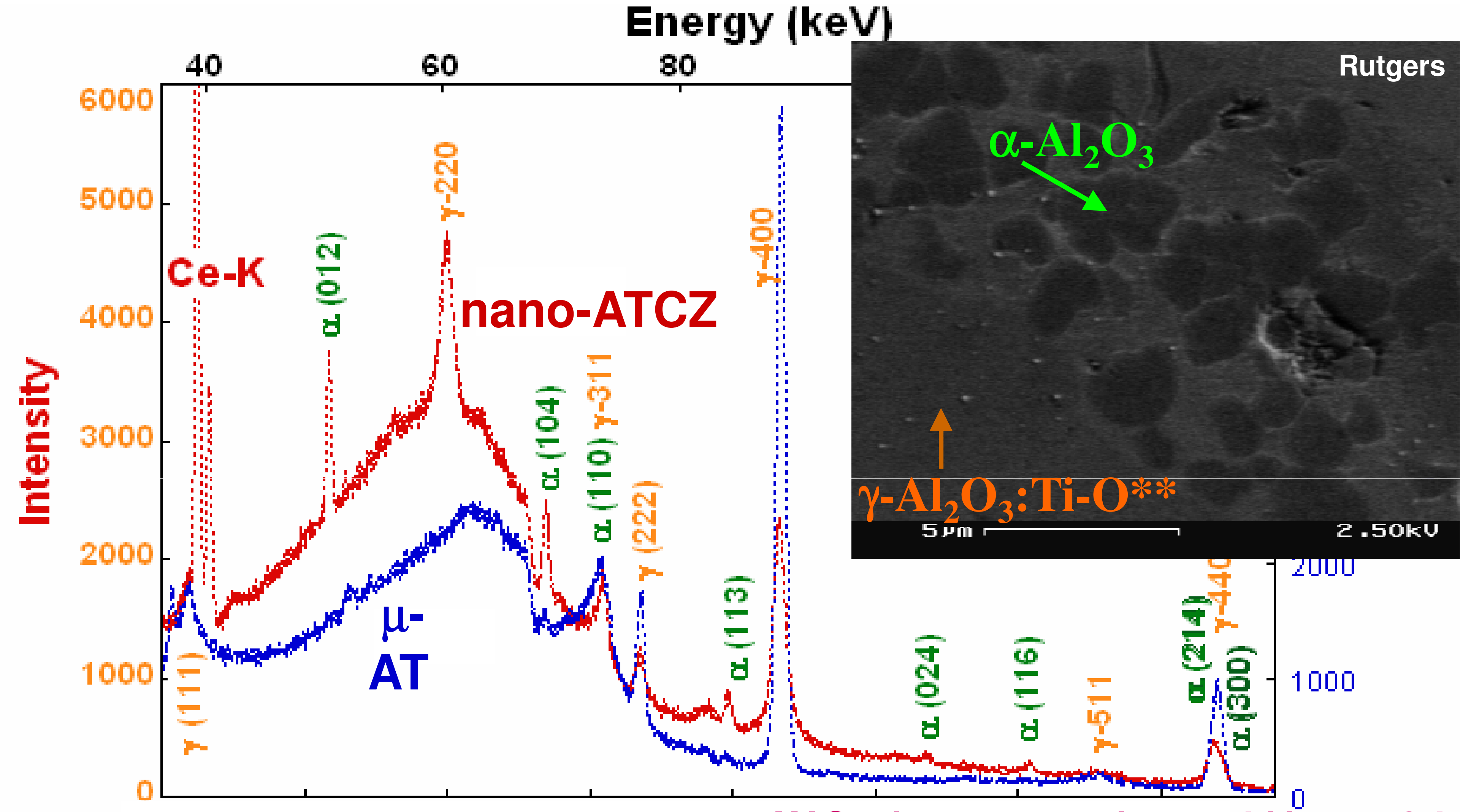
nano-coating

stronger α-Al_2O_3 : corundum lines / content

amorphous content larger

EDXRD –structure

Coatings: delaminated & powdered



XAS micro-nanoprobe would be useful

nano-coating

stronger α-Al_2O_3 : corundum lines / content

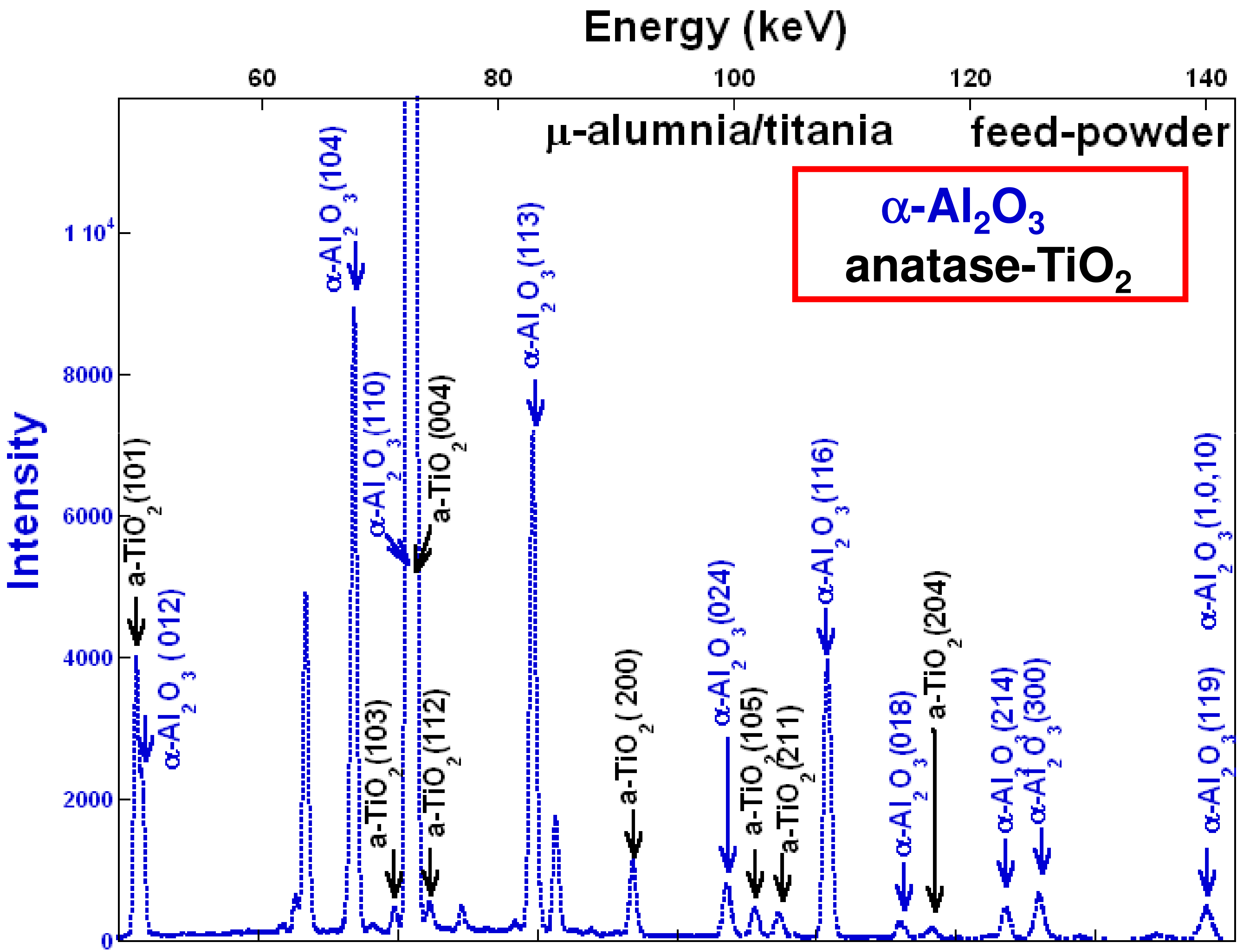
amorphous content larger

** U.-Conn. Group electron microscopy: Ti in γ-Al_2O_3

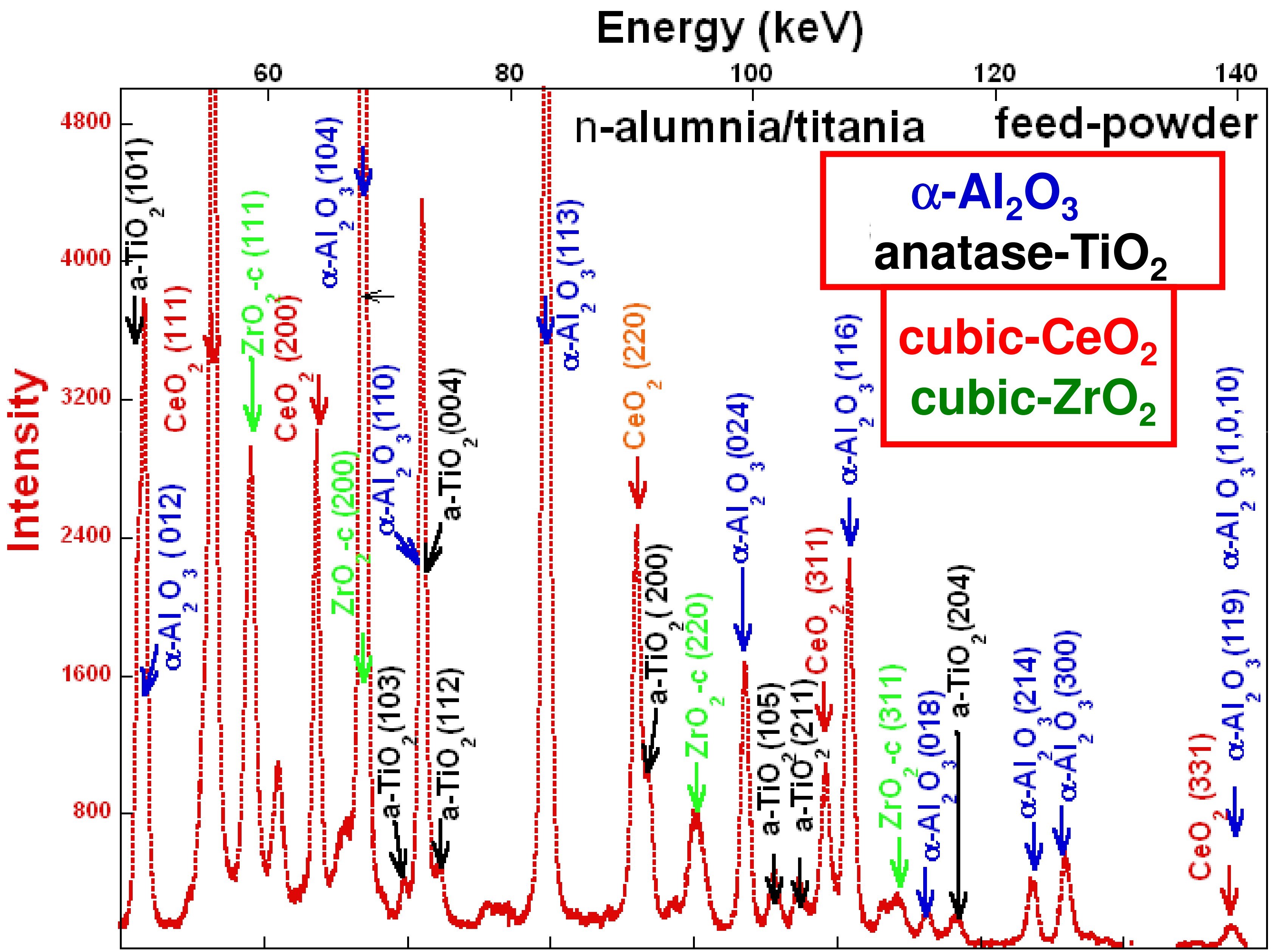
Goberman, Sohn, Shaw,Jordan, Gell. Acta Mat. 2002;50:1141.

Bansal et. al. Acta Mat. 51 (2003) 2959–2970:

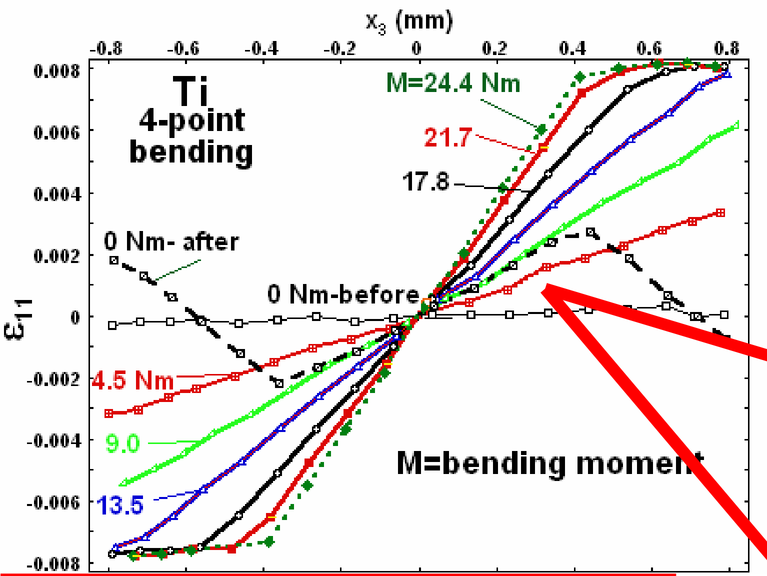
EDXRD –structure **μ-alumina/titania feed powder**

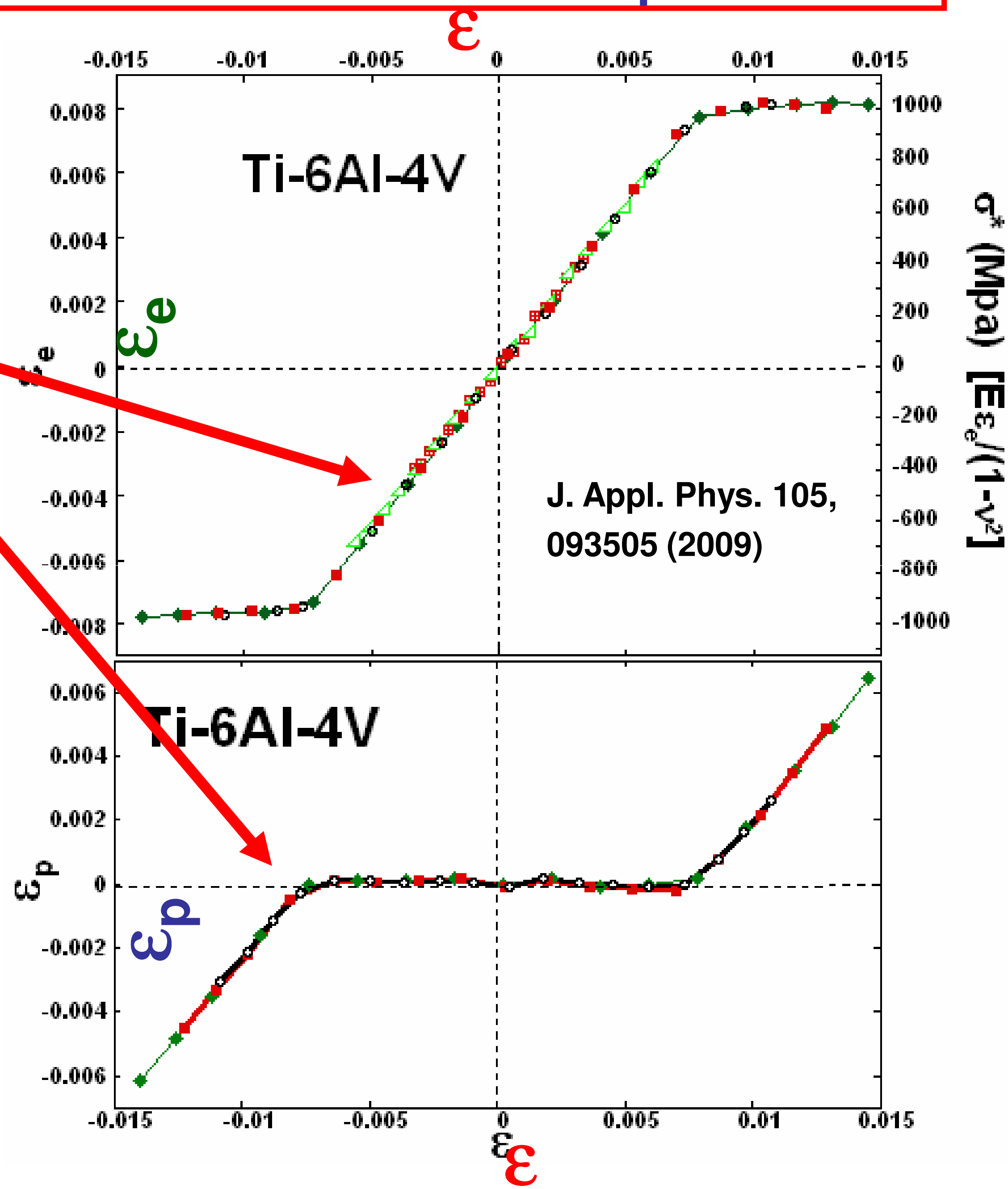


EDXRD –structure **nano-alumina/titania feed powder**



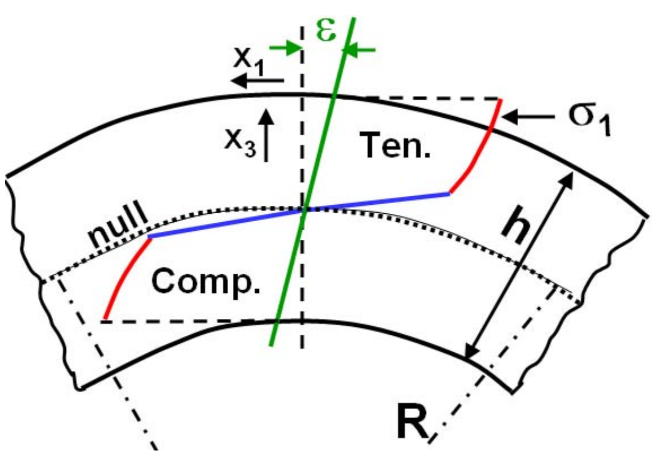
All data collapse to universal curves in ε_e or ε_p vs. ε !!





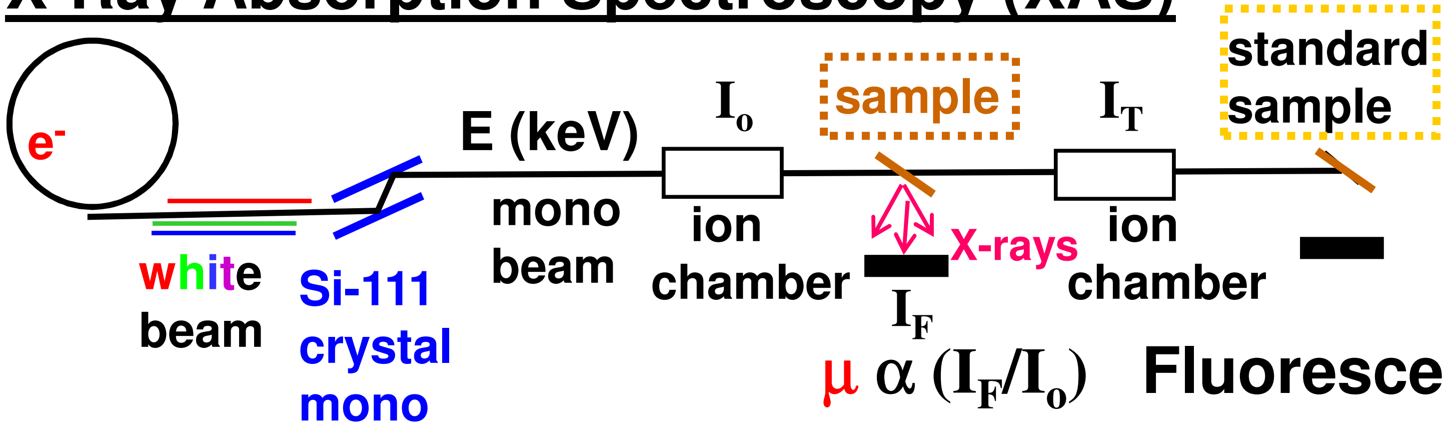
calculate measure extract

$$\varepsilon = \varepsilon_e + \varepsilon_p$$

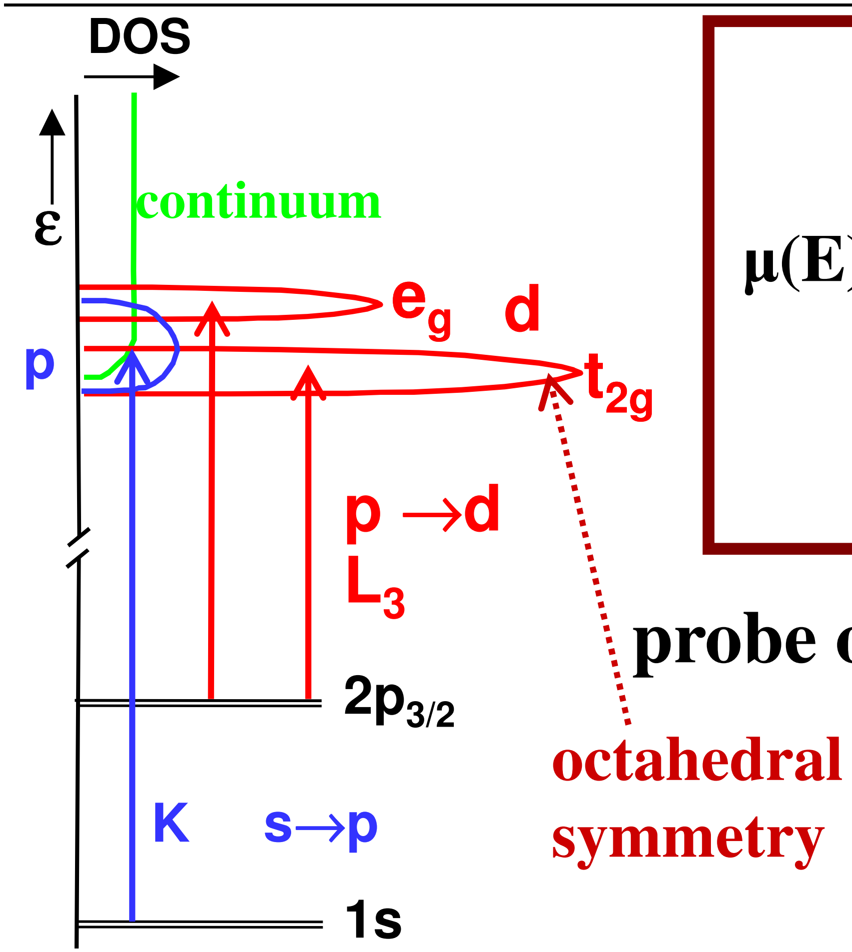


X-Ray Absorption Spectroscopy (XAS)

Simple Exp. Techniques



$\mu \; \alpha \; (I_F/I_o)$ **Fluorescence XAS**



Fermi Golden Rule

dipole/quadrupole operator

$$\mu(E) = \sum_{\text{final states}} \rho(E_f)\left|\langle \Psi_f \,|\, \hat{H} \,|\, \Psi_i \rangle\right|^2$$

f = empty states

i = core level

XAS : hole state spectroscopy

probe of empty states above Fermi level

Atom (element) specific centered probe (inside out view !!!)
- electronic & “crystal” structure

Powerful

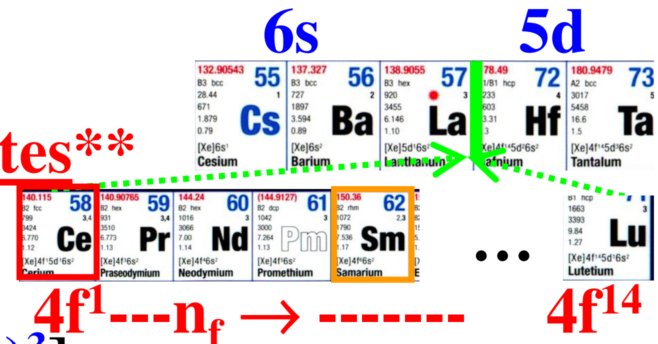
---

powders, single crystals, very-very low concentration impurities, very thin films (sub-monolayer), liquids, colloidal suspensions, amorphous materials ...

Versatile

XAS micro-(NSLS)/nano(NSLS-II)- probe:
local mapping of structure chemistry

Ce Problem and Ce-L_3 valence (special case)



Rare Earth (RE) 4f -localized atomic, core states**

Ce – first RE

Energy of Ce^{4+}:[$4f^0$ $(5d6s)^4$] ≅ Ce^{3+}:[$4f^1$ $(5d6s)^3$]

{** Ce borderline 4f- localized 4f – itinerant}

{** n_f < ~3.3}

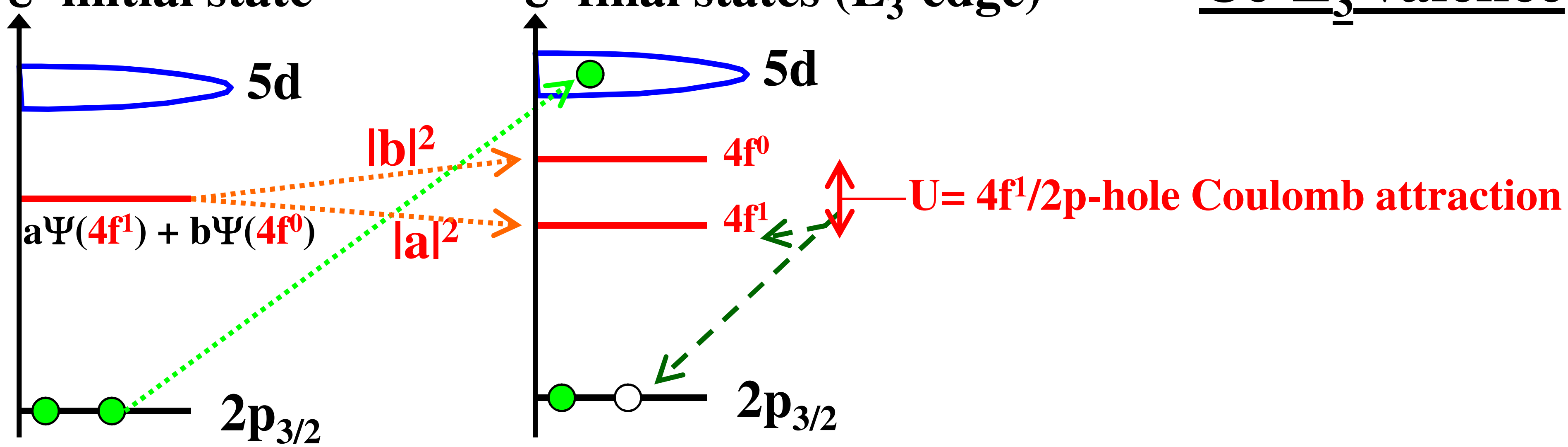
Often mixed-valent ($v=4-n_f$) Ce solid state ground state

$$\Psi_{GS} = a\Psi(4f^1) + b\Psi(4f^0) \qquad Ce^{[4-n_f]+} : 4f^{n_f} \qquad 0 \le n_f = |a|^2 < 4$$

ε initial state

ε final states (L_3-edge)

Ce-L_3 valence



L_3 XAS Ce-valence determination $\{Ce^{3+/4+}, Sm^{3+/4+}, Eu^{3+/4+}, Tm^{3+/4+}, Yb^{3+/4+}\}$

mixed-valent Ce ground state

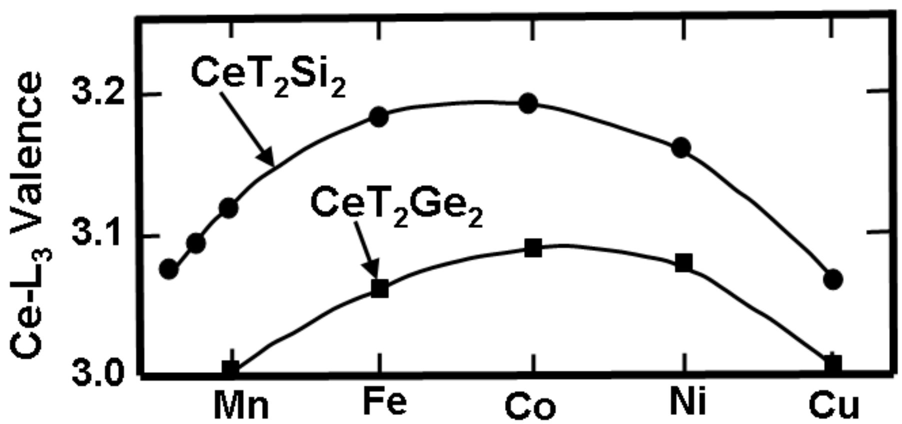
$$\Psi_{GS} = a\Psi(4f^1) + b\Psi(4f^0)$$

Ce^{3+} Ce^{4+}

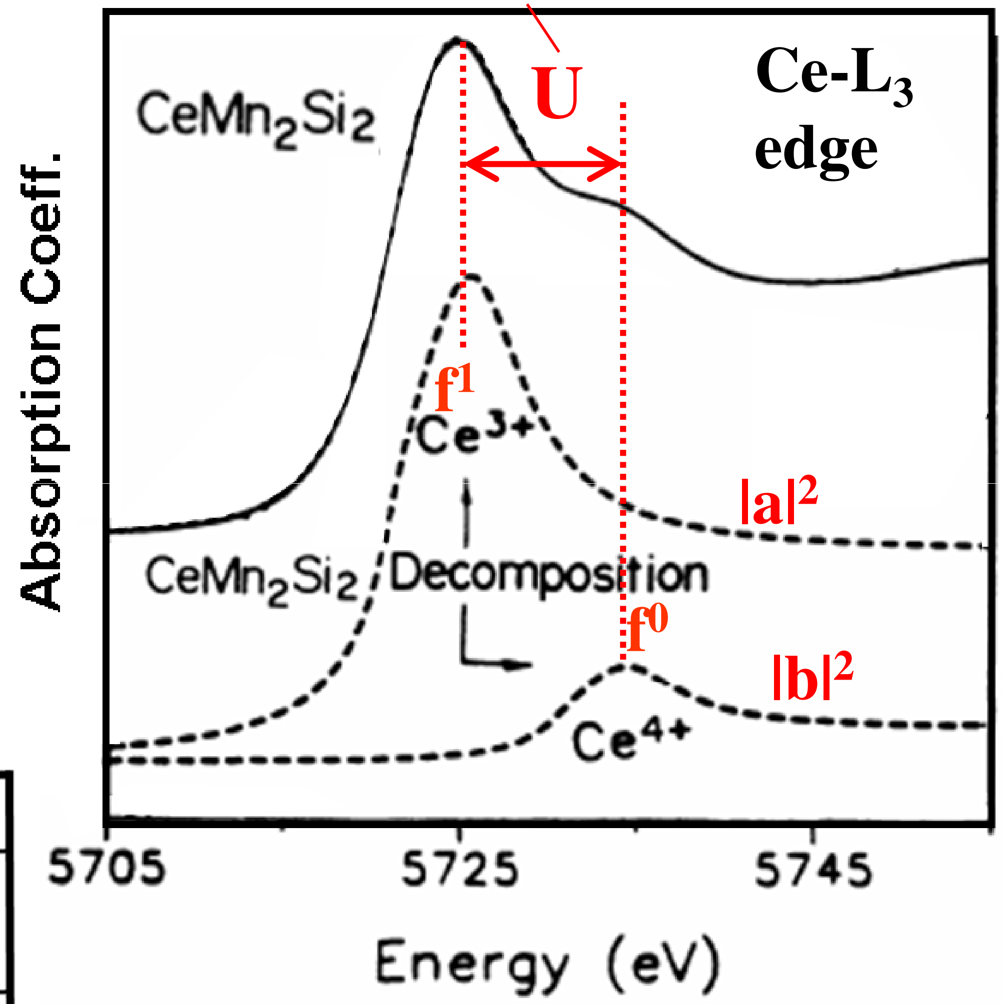
Valence (L_3)=4-n_f= 4-$|a|^2$

Ce- L_3 valence

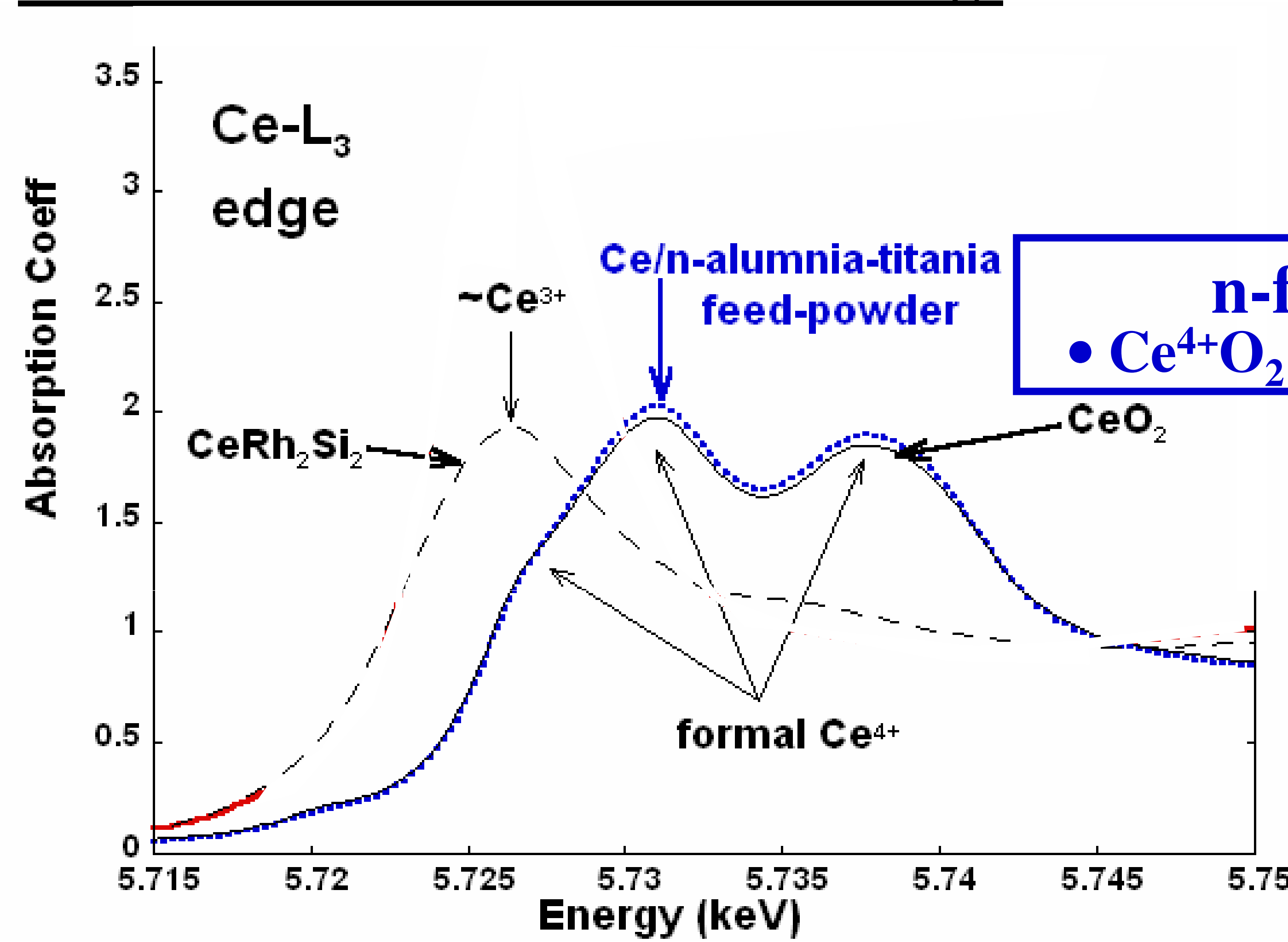
- **exquisitely** sensitive probe of local chemistry !!



U= $4f^1$/2p-hole Coulomb attraction



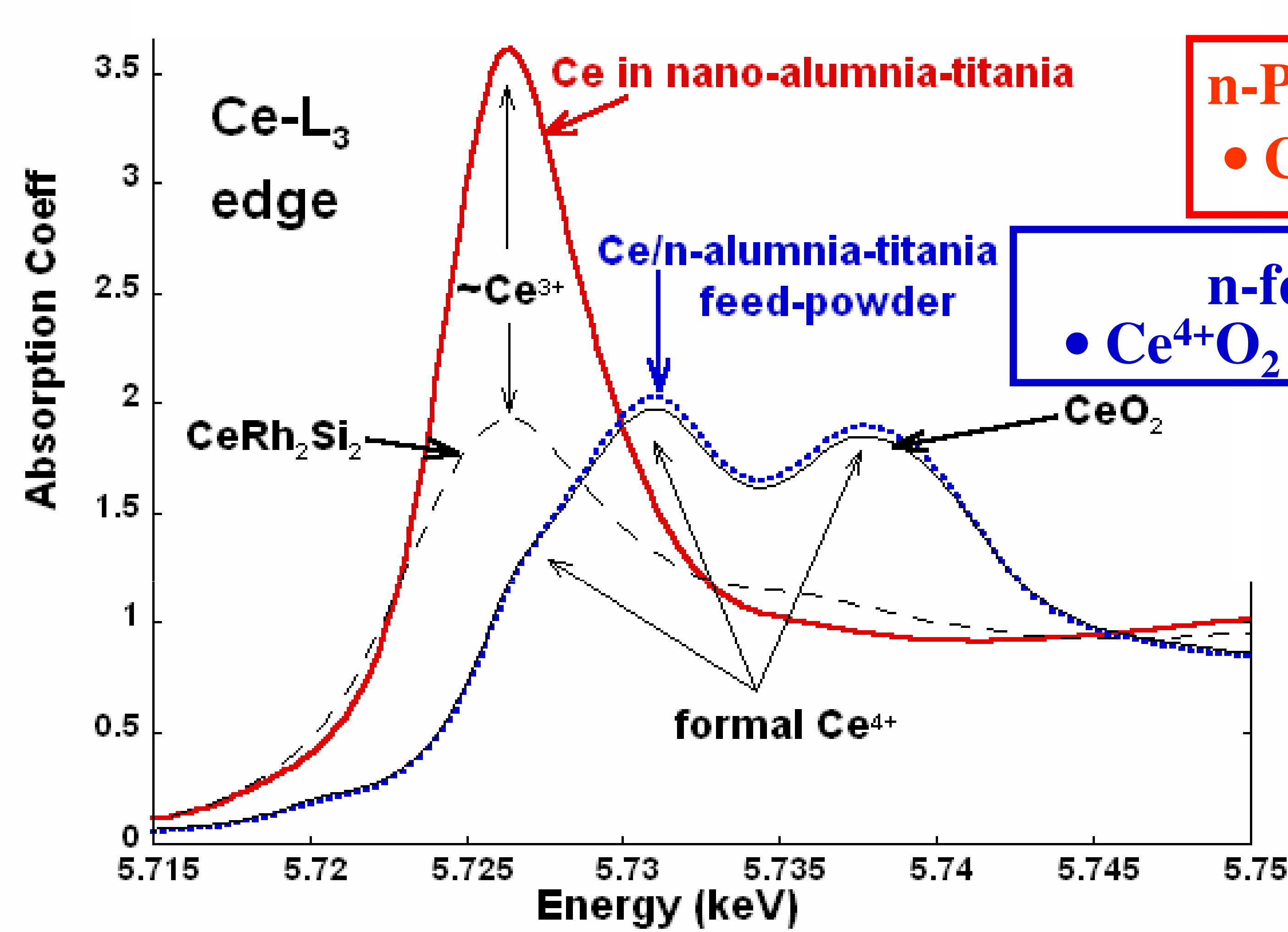
Ce in nano-alumnia-titania PS coatings



n-feed powder

- $Ce^{4+}O_2$ fluorite structure

Ce in nano-alumnia-titania PS coatings



n-PS coating
- Ce^{3+}

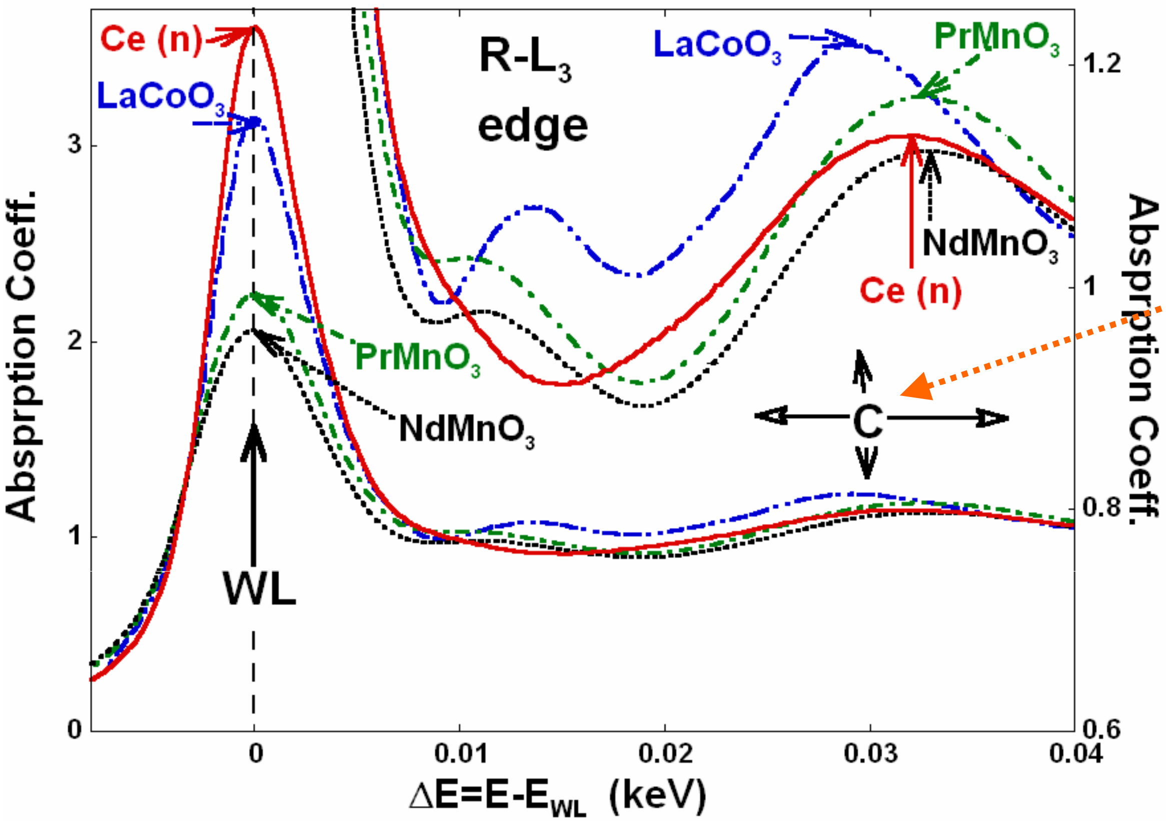
n-feed powder
- $Ce^{4+}O_2$ fluorite structure

$$Ce^{4+}O_2 \xrightarrow{PS} Ce^{3+} \text{ !!!!!!}$$

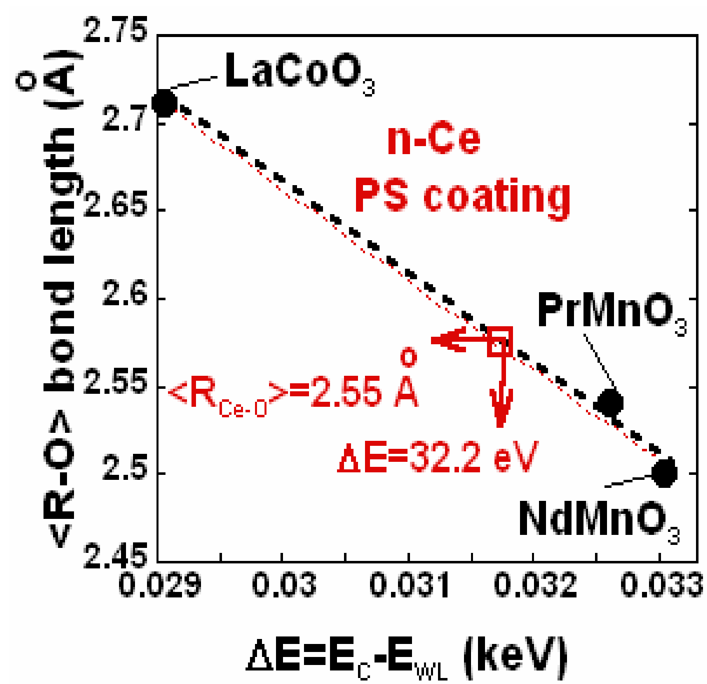
Plasma Spray
Chemical reduction of Ce

Average Ce-O distance estimate

Rare Earth continuum resonance "C" feature energy or Natoli's rule: *kr* = const



Regular shift with R-O distance



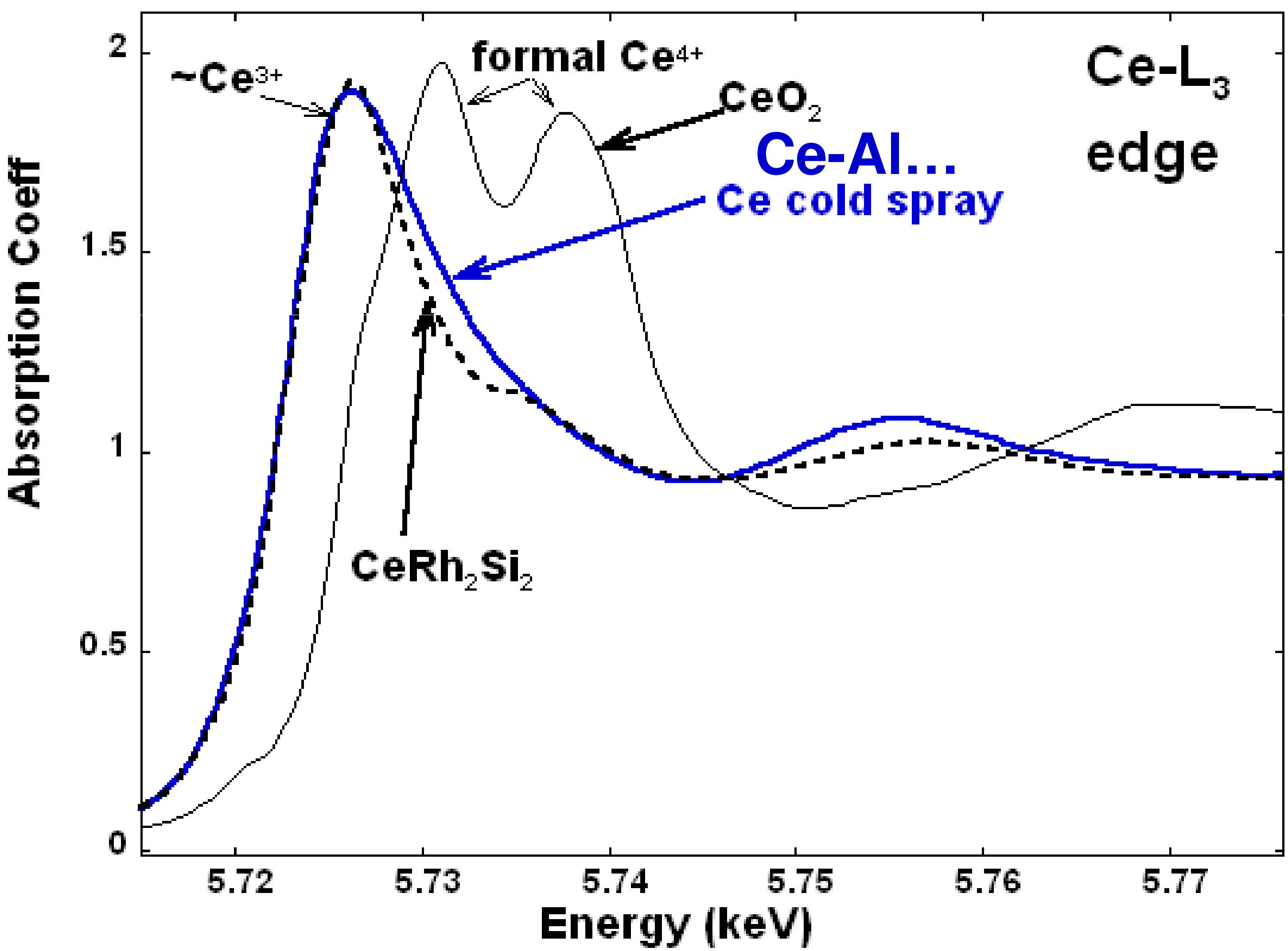
$\langle R_{Ce\text{-}O} \rangle = 2.55$ Å
consistent with Ce^{3+}

Aside **Ce-Al… cold spray (George Kim & coworkers)**

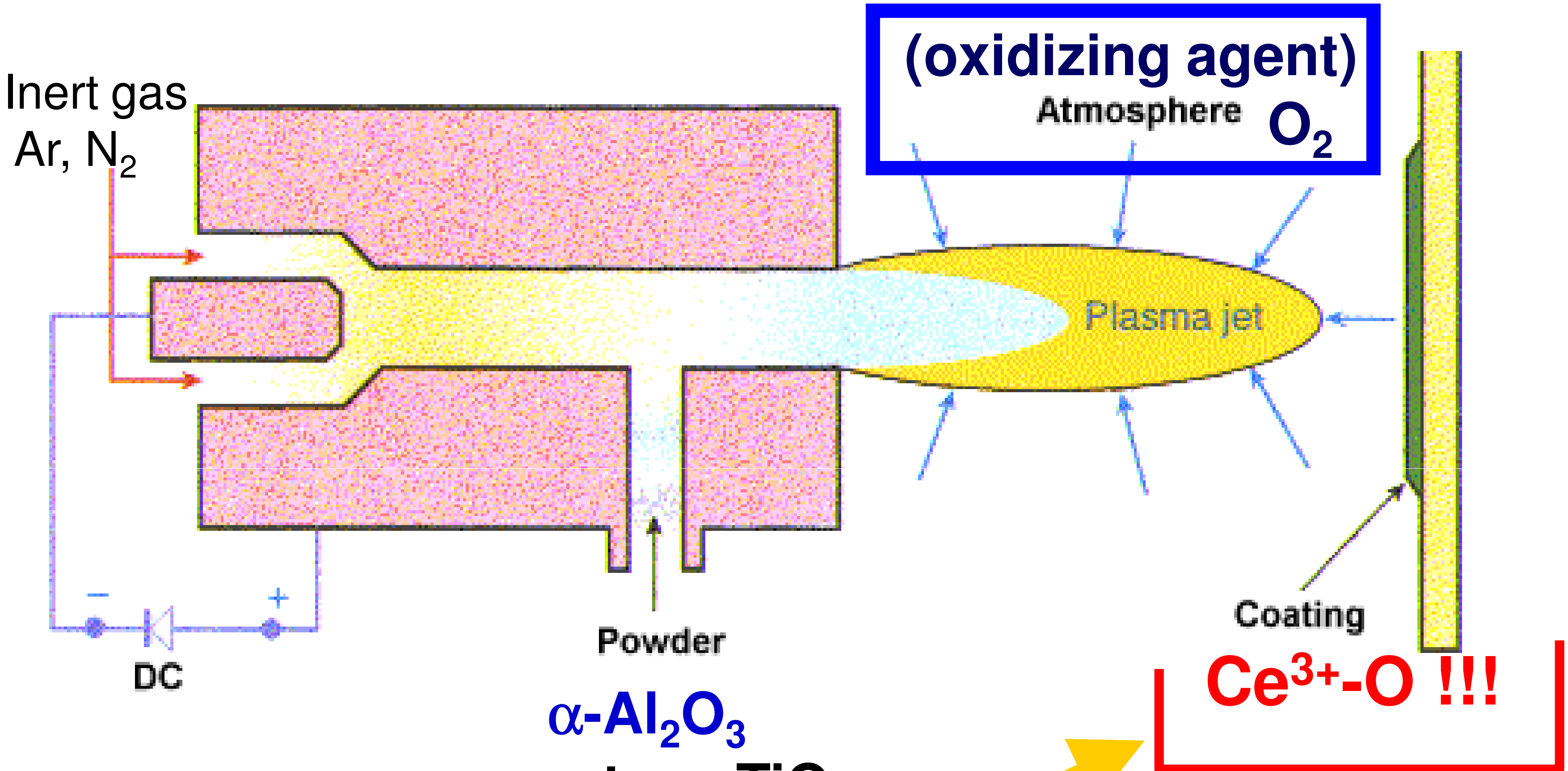
Ce^{3+} typical of Ce-Al inter-metallics

CeAl, $CeAl_2$, $CeAl_3$, Ce_3Al_3

Very stable against oxidation, very hard



Plasma spray deposition



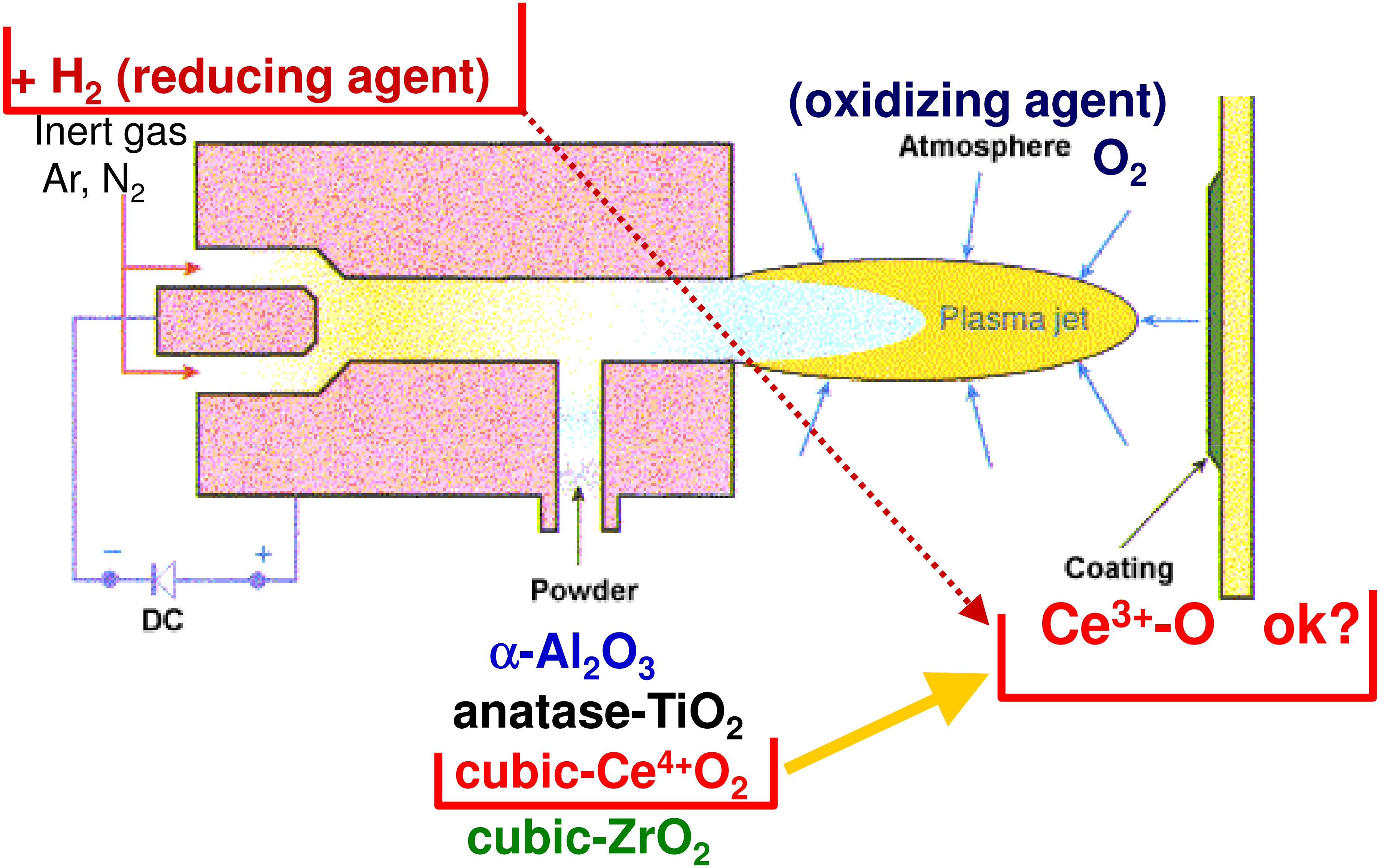
α-Al_2O_3

anatase-TiO_2

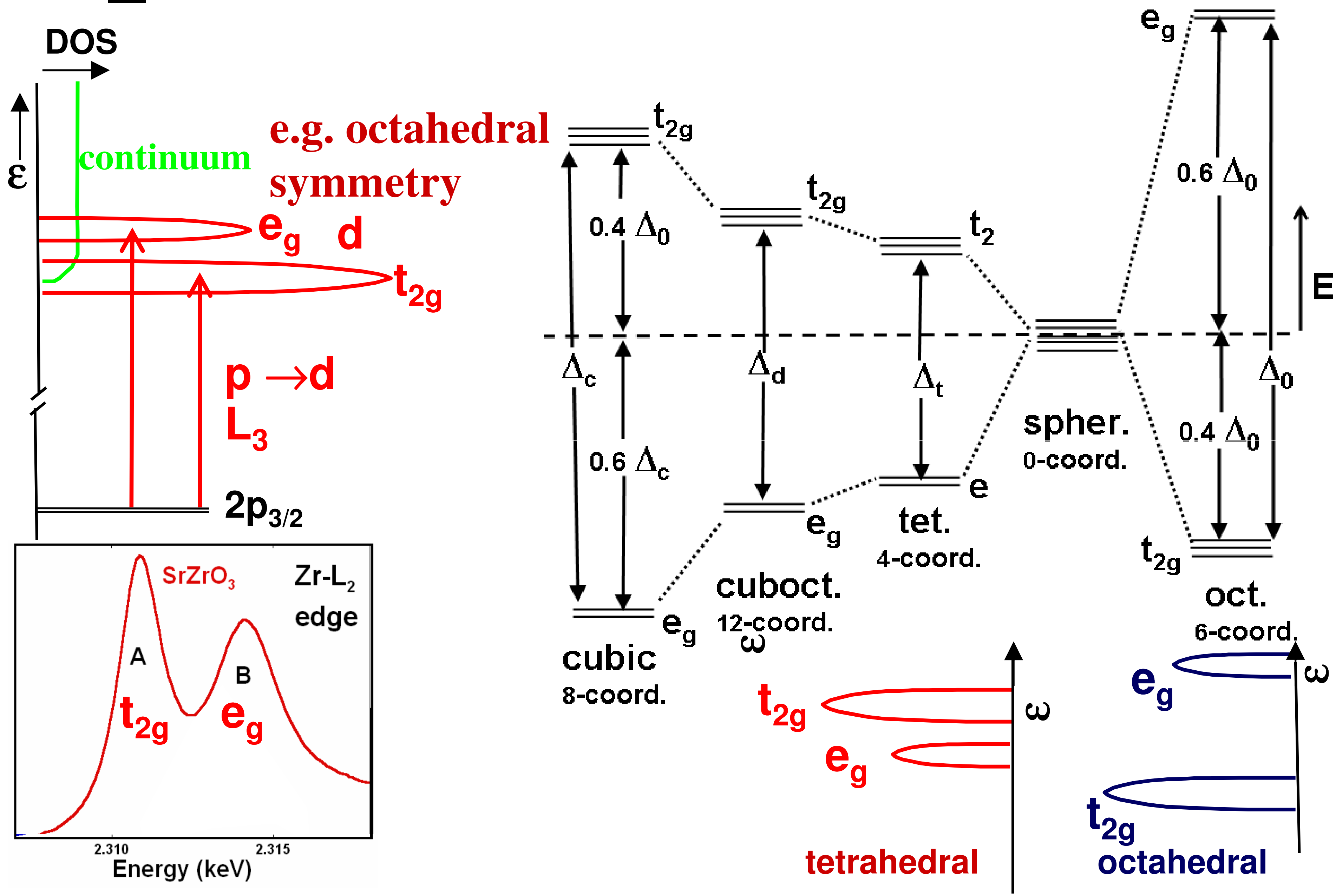
cubic-$Ce^{4+}O_2$

cubic-ZrO_2

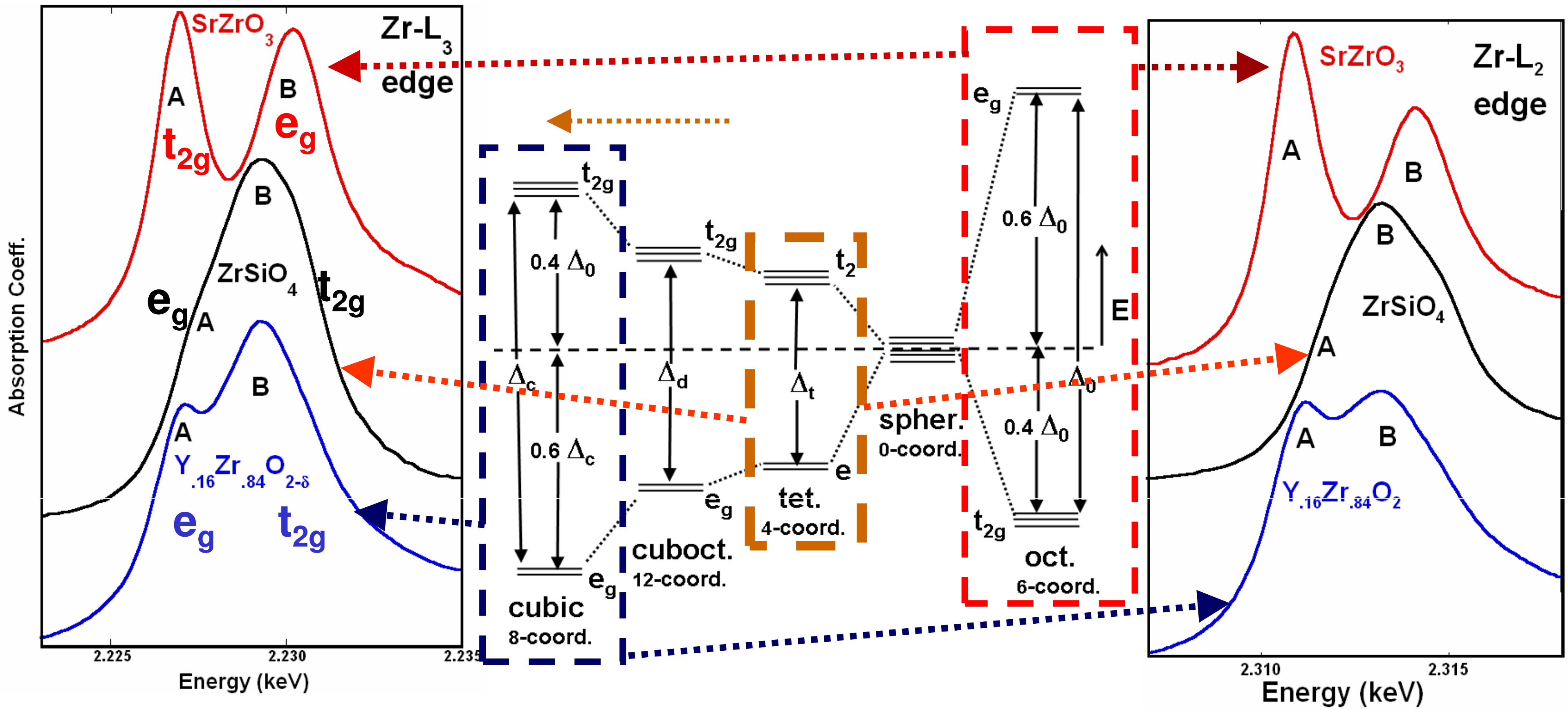
Plasma spray deposition



Zr $L_{2,3}$-edge probe of local electronic structure: ligand coordination



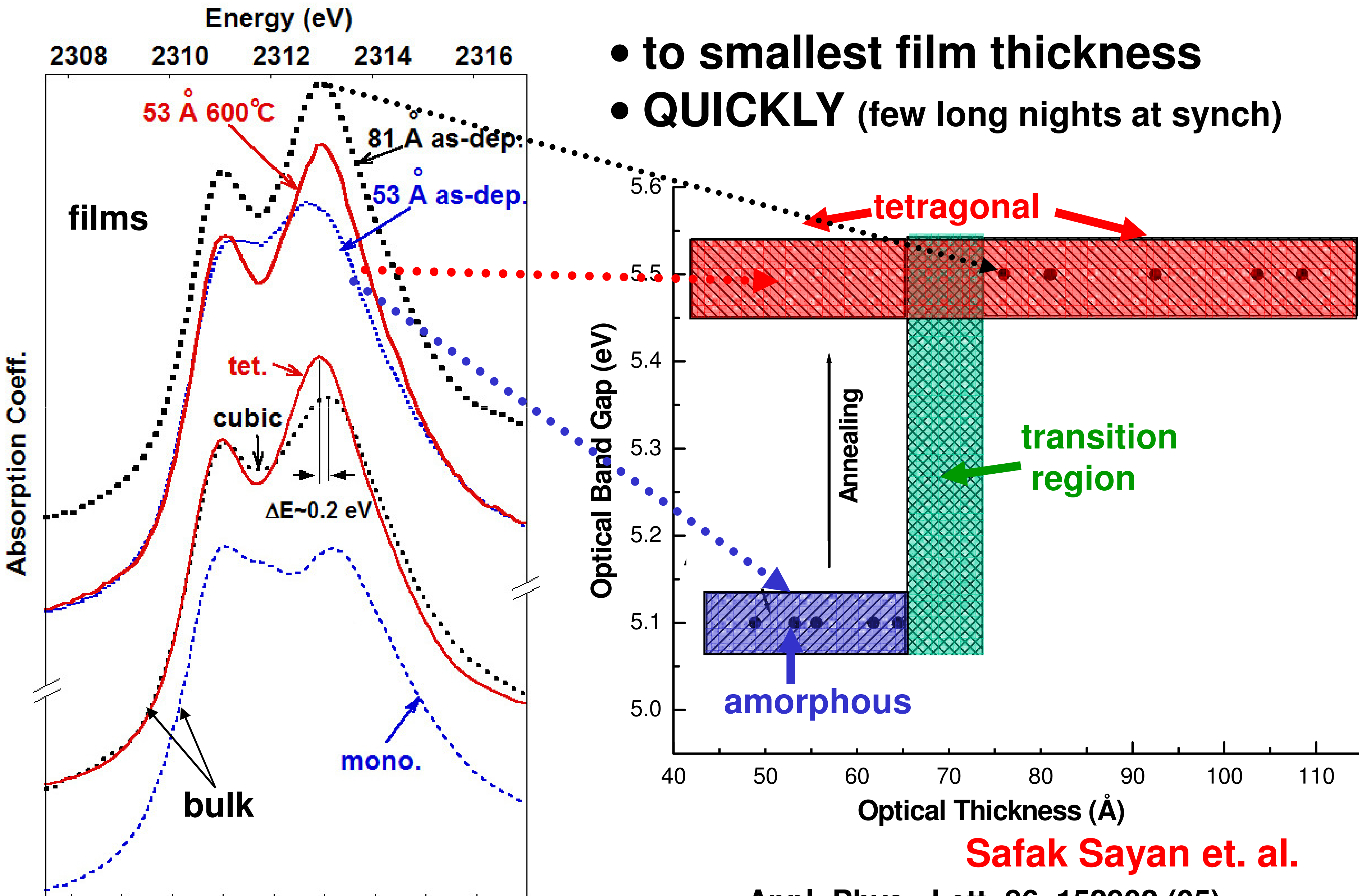
Zr $L_{2,3}$-edge probe of local electronic structure: ligand coordination



Zr-L_3 XAS – on nanoscale structures example

electronic structure to map crystal structure in processing space

- to smallest film thickness
- **QUICKLY** (few long nights at synch)



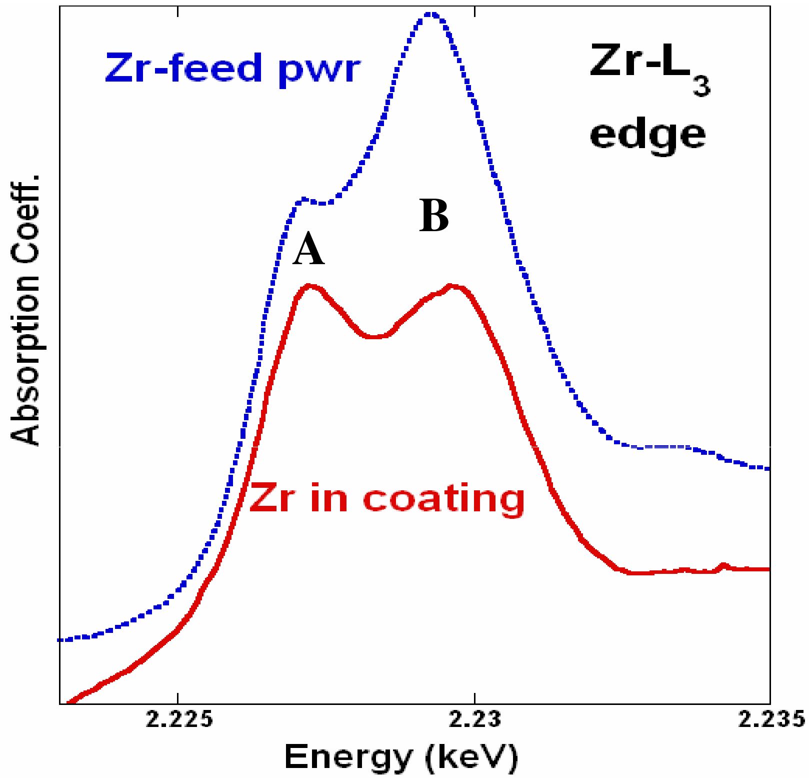
Safak Sayan et. al.

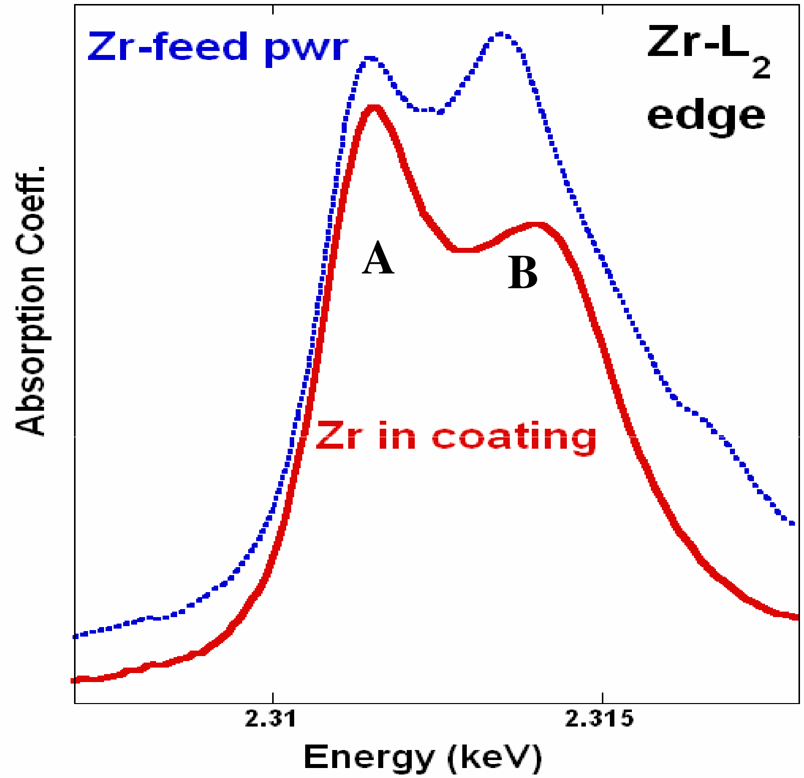
Appl. Phys. Lett. 86, 152902 (05)

Zr in nano-alumnia-titania PS coatings

- Zr in nano-alumnia-titania feed powder

  local **cubic** symmetry = ZrO_2 …



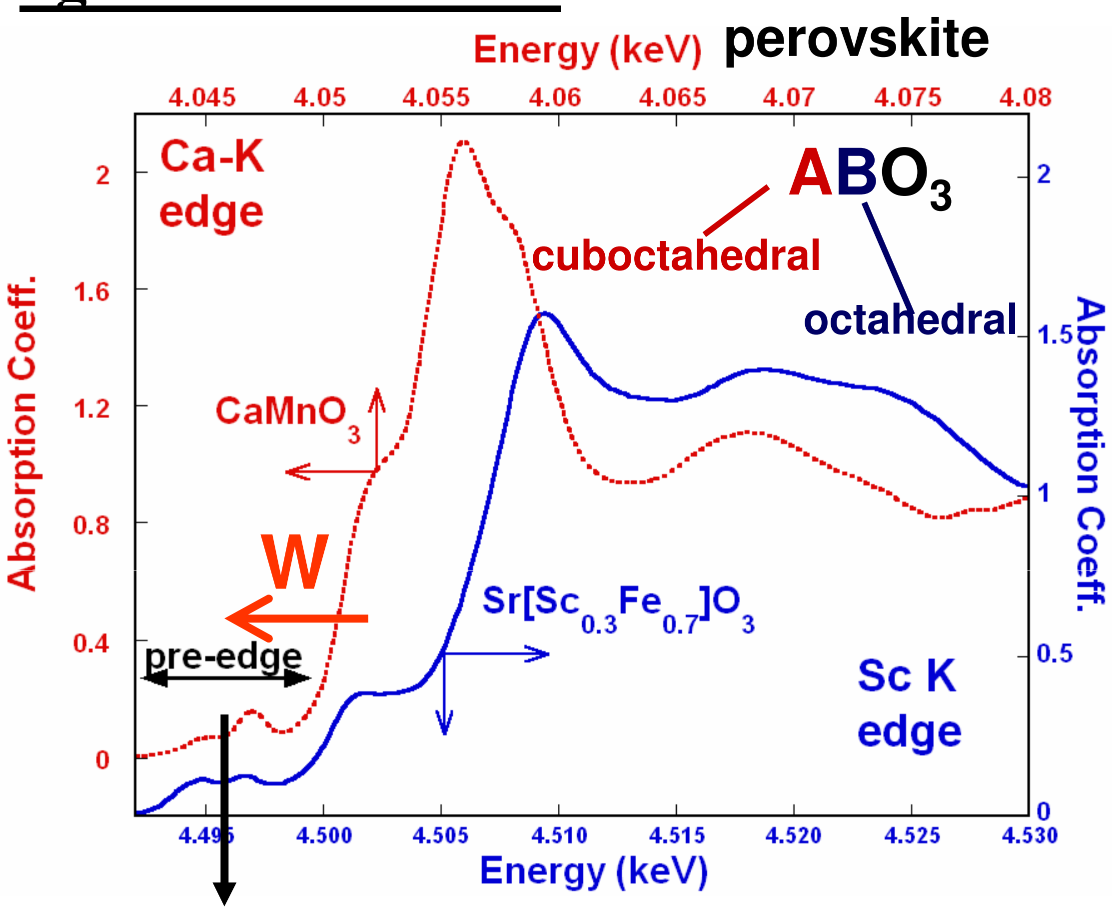


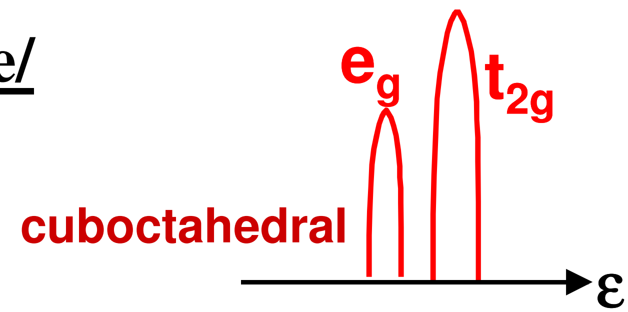
- Zr in nano-alumnia-titania PS coating

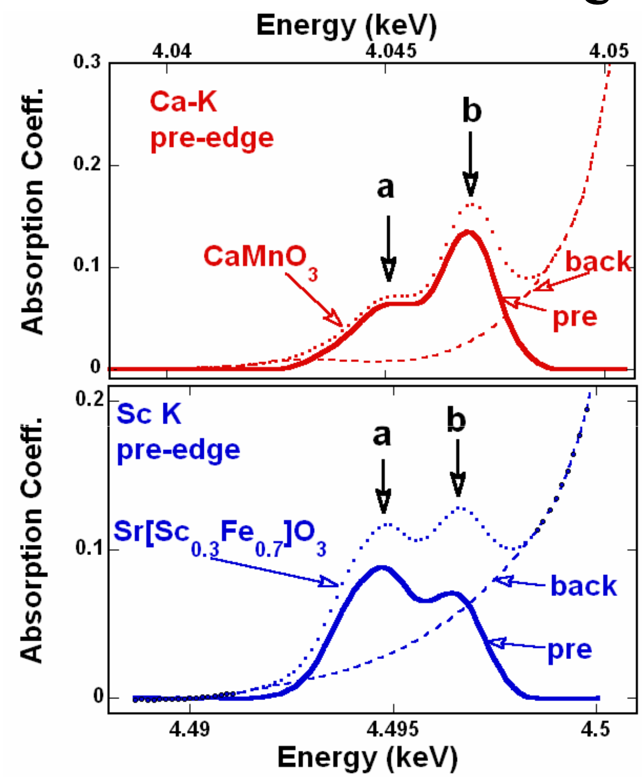
  local **octahedral** symmetry = ZrO_2

- cubic $\xRightarrow{\text{PS}}$ octahedral

T(3d)-K pre-edge: local electronic-structure/ ligand-coordination



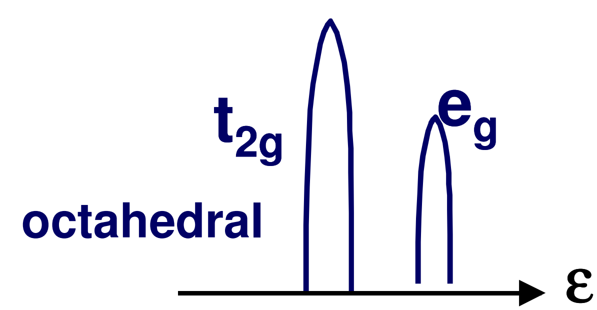




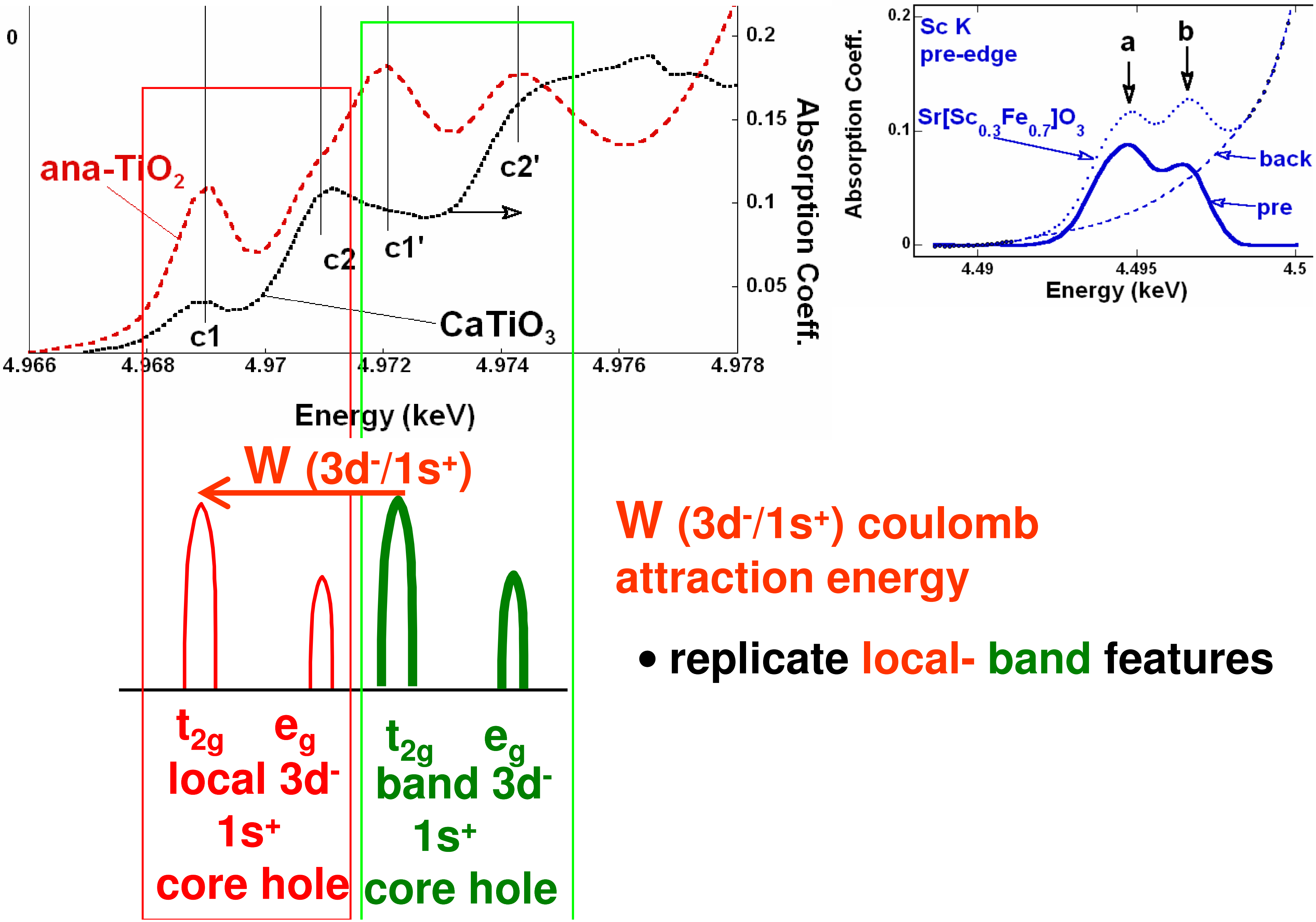
- **Final state s-core-hole/d attraction energy W**
- **transitions**

  quadrupole s→d (much weaker)

  + dipole s →d/p-hybridized (variable)



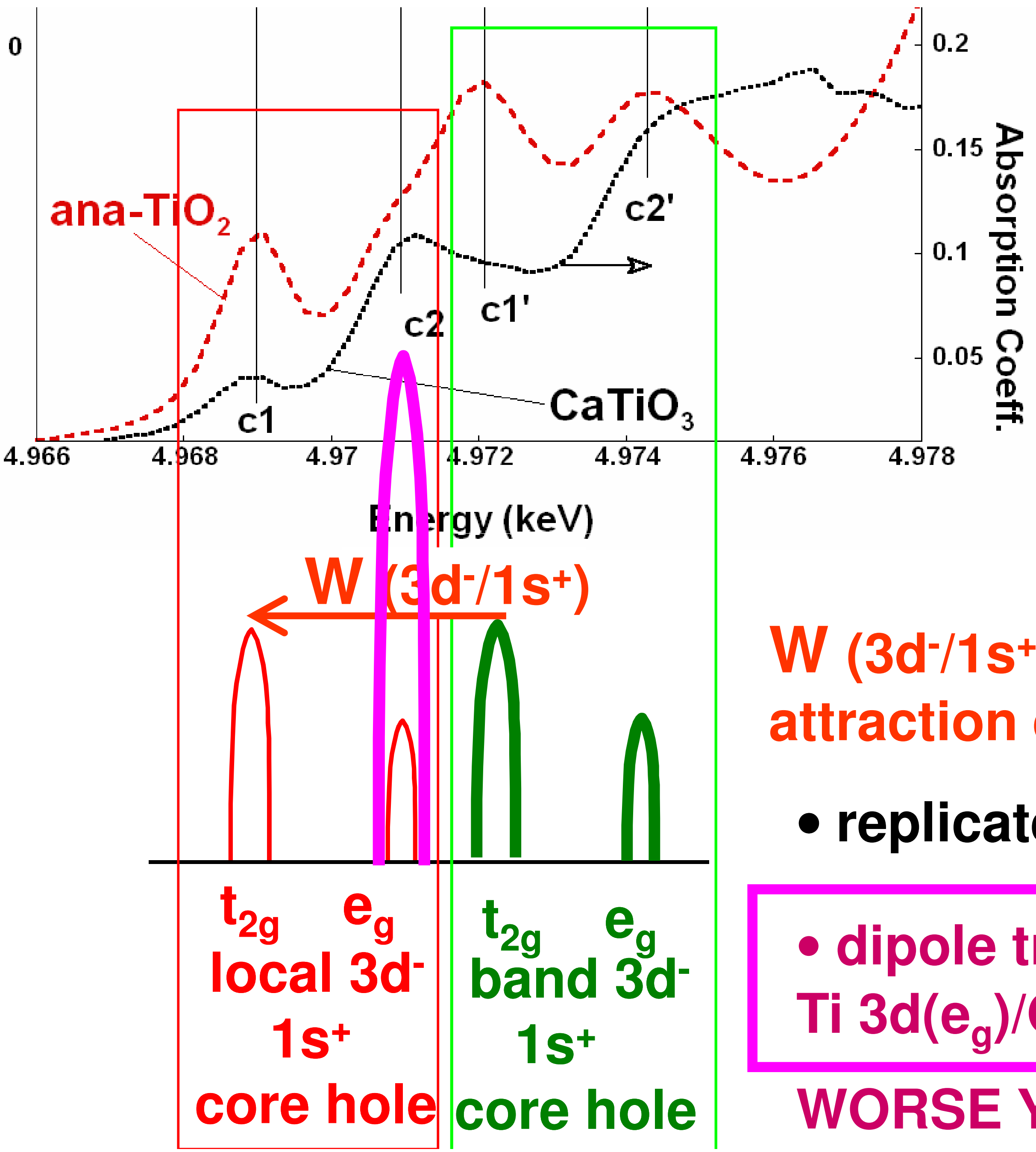
T(3d)-K pre-edge: local electronic-structure- life more complex

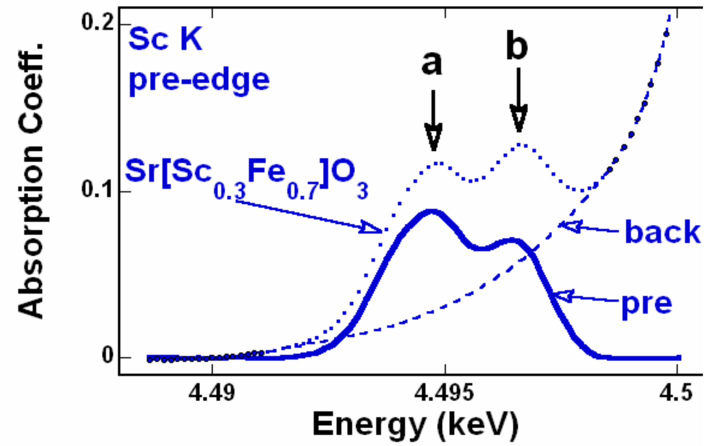


W ($3d^-/1s^+$) coulomb attraction energy

- replicate local- band features

T(3d)-K pre-edge: local electronic-structure- life more complex





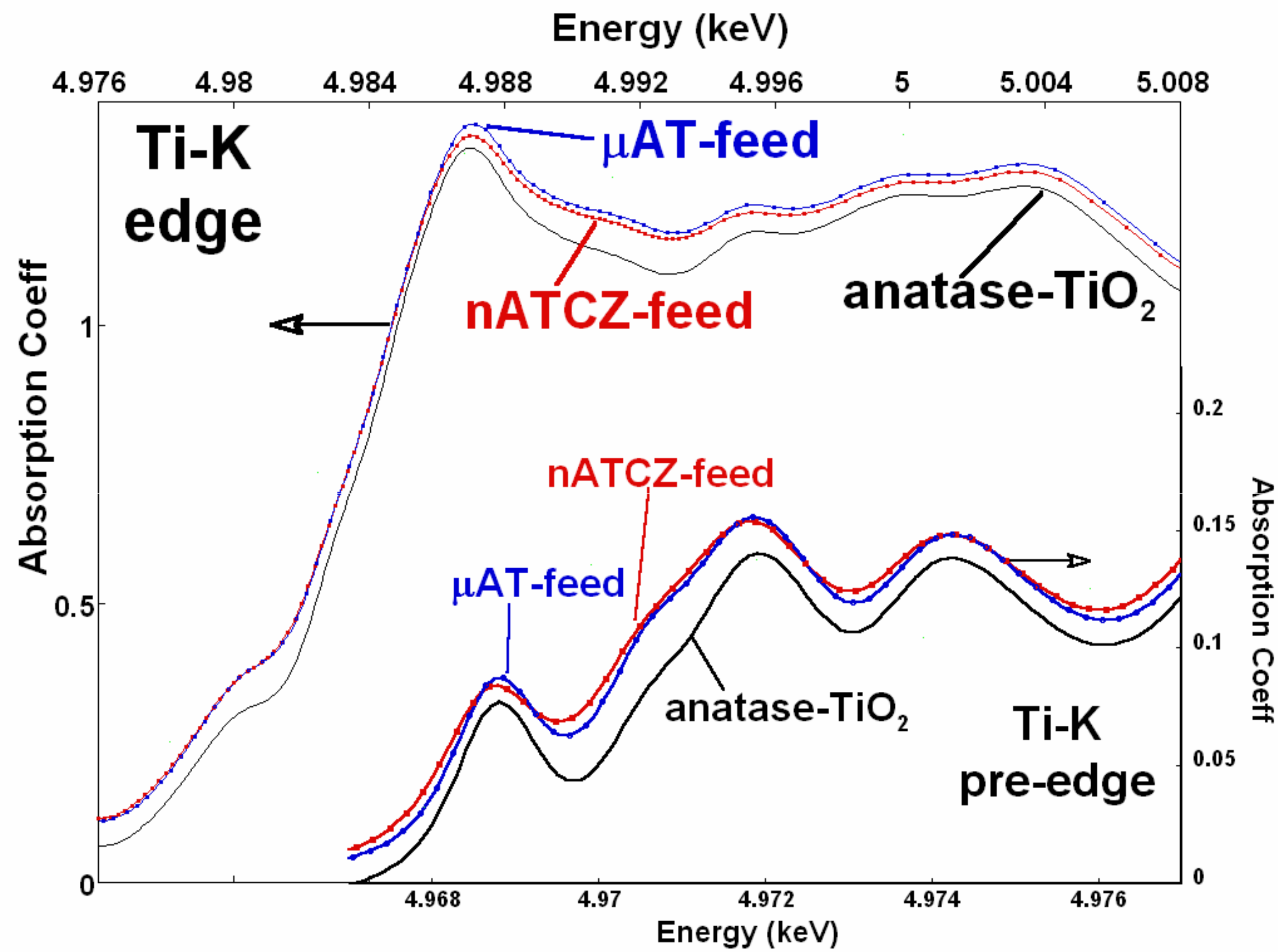
W $(3d^{-}/1s^{+})$ coulomb attraction energy

- replicate local- band features

- dipole transitions to Ti $3d(e_g)/O(2p)$ hybrid states

WORSE YET

Ti in feed powder micro-aluminia-titania (μAT)
nano-aluminia-titania-ceria-zirconia (nATCZ)

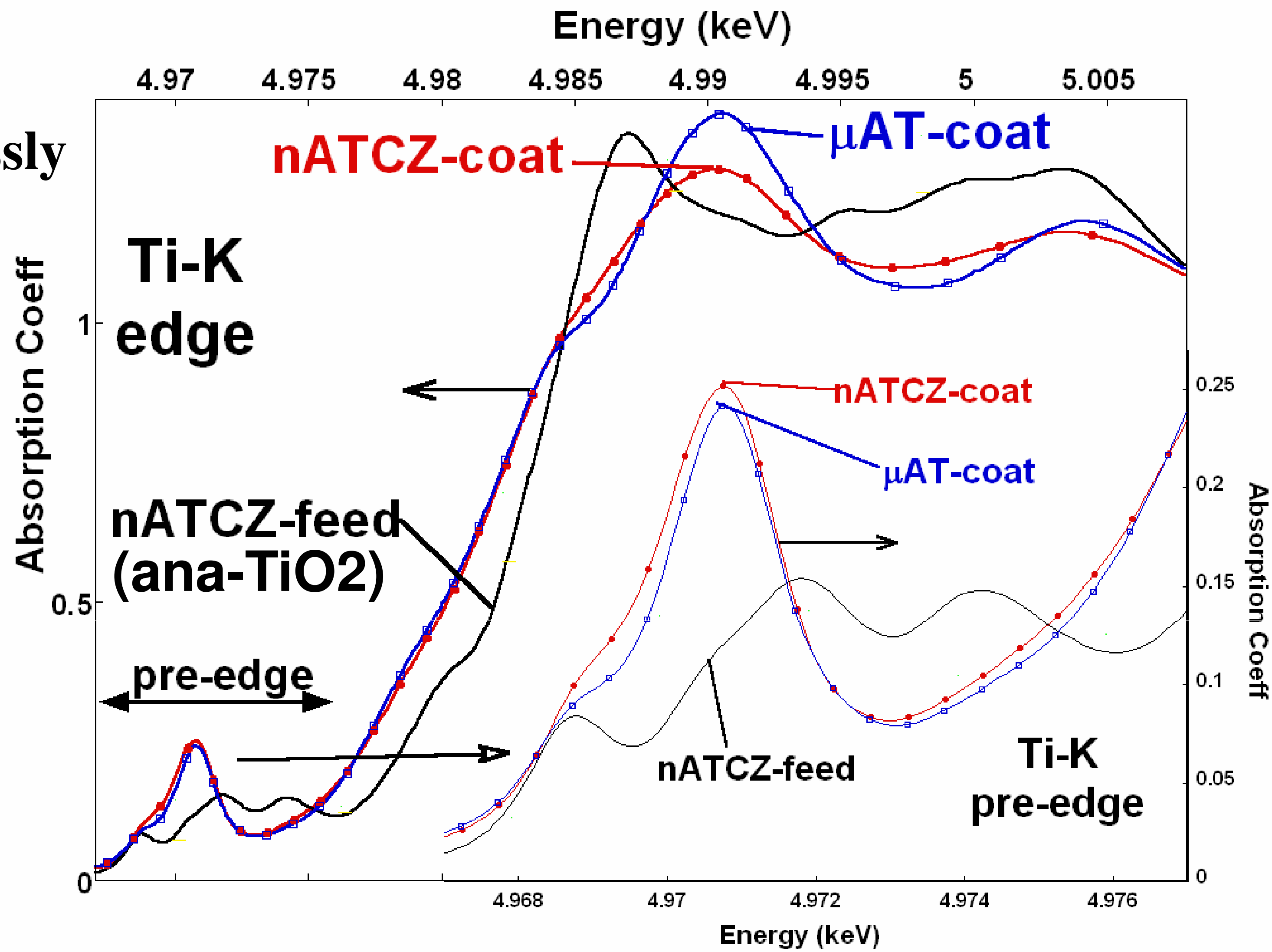


• feed powder μAT = nATCZ = anatase phase TiO_2

Spectral fingerprint

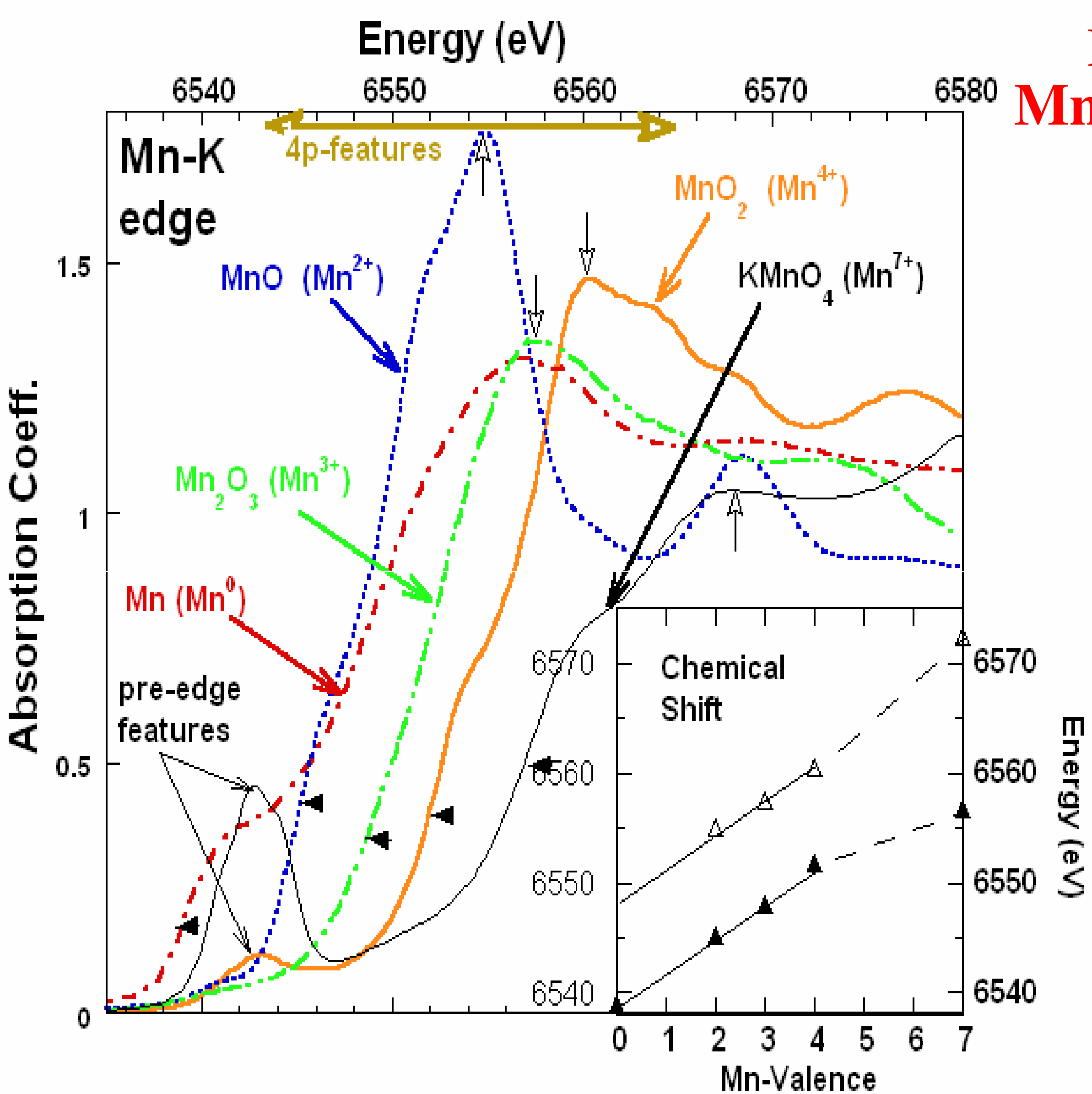
PS coatings

- coatings grossly different structure from ana-TiO_2



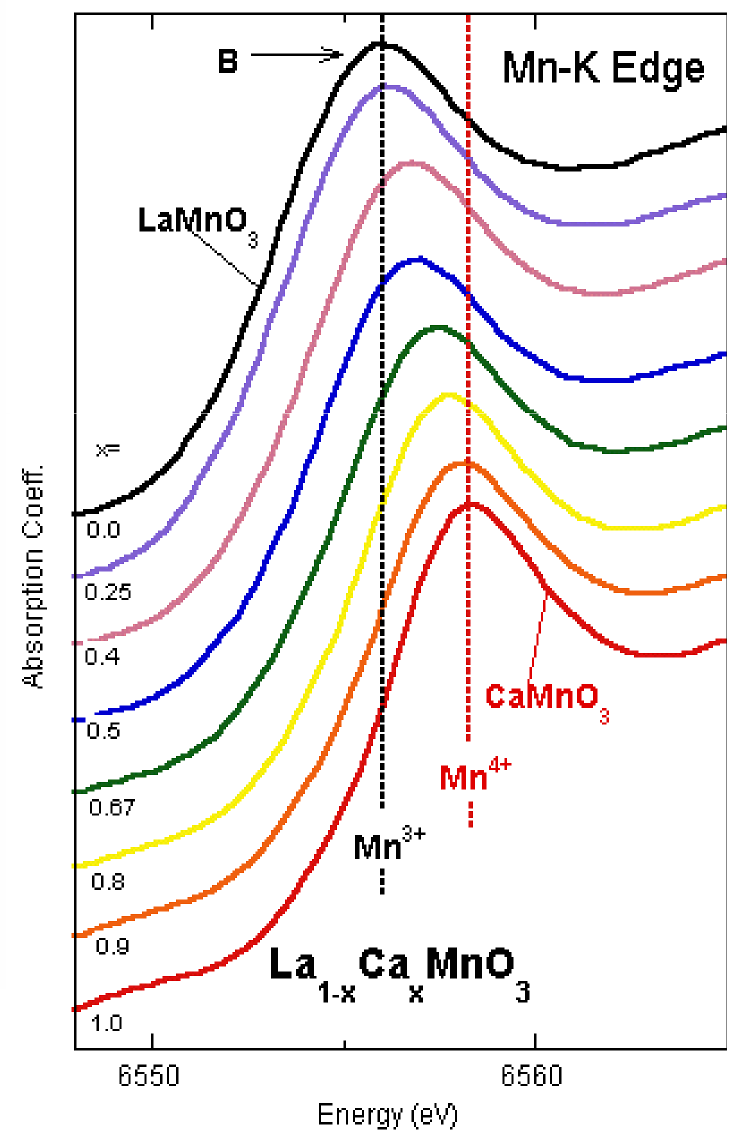
- PS coating quite similar for μAT & nATCZ
- nATCZ PS coating spectrum **broadened ⇒ atomic disorder**

XAS chemical shift of main edge to higher energy with higher valence



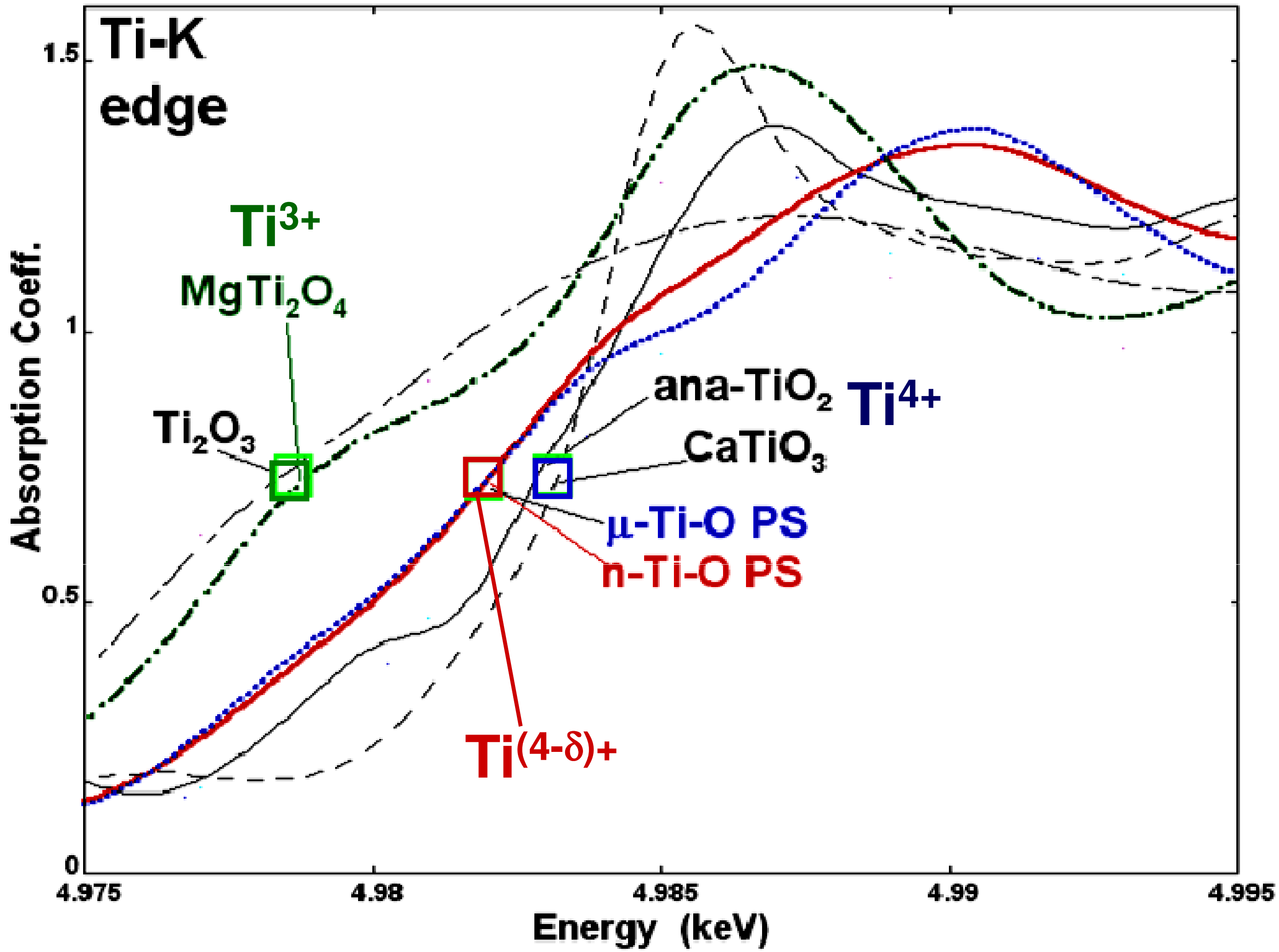
$La^{3+}_{1-x}Ca^{2+}_{x}Mn^{3+/4+}O_3$

Mn-K-XAS → key Mn^{3+}/Mn^{4+}



Mn^{N+}: e^- states more tightly bound as N↑

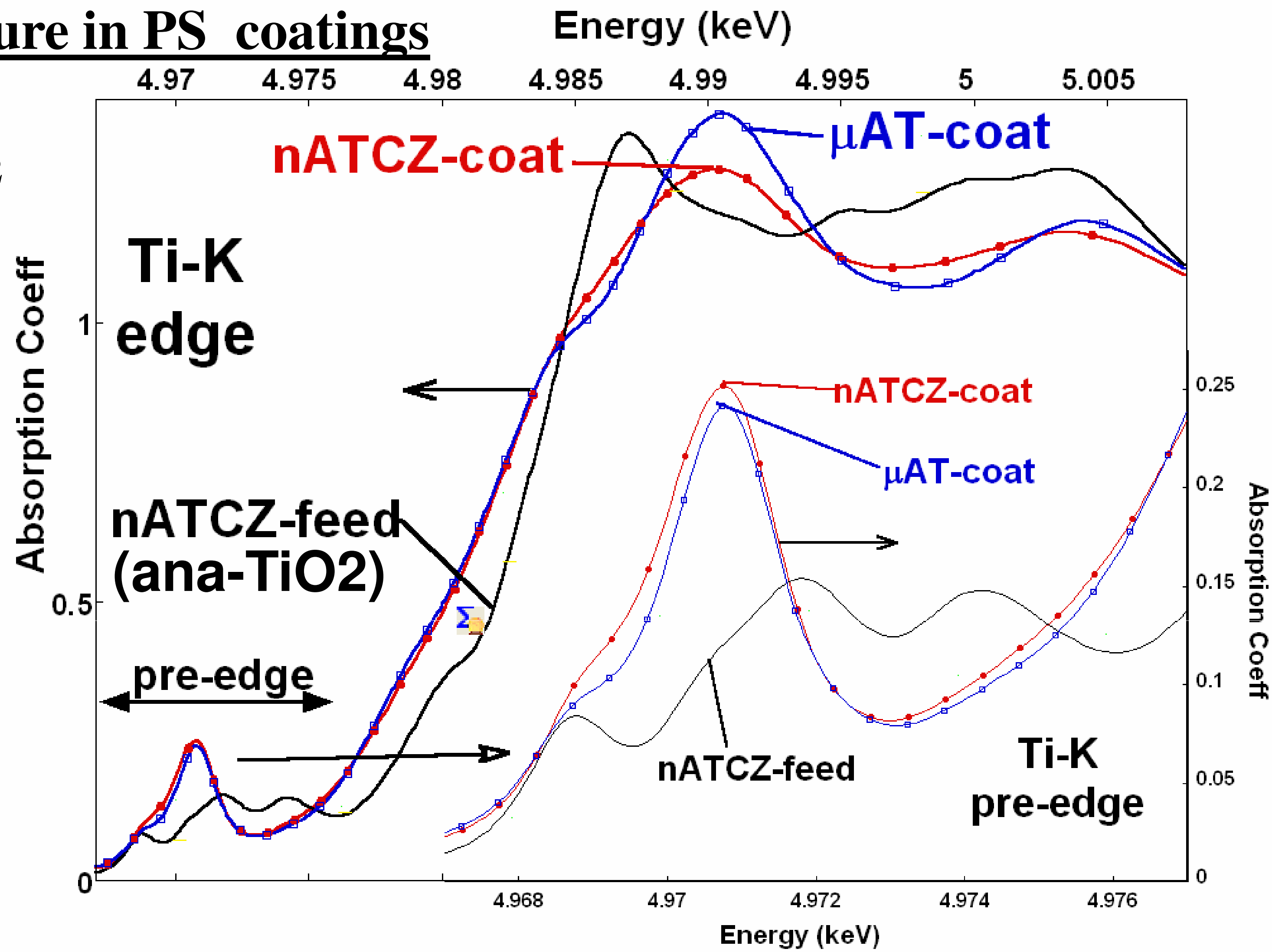
Ti-valence state in aluminia-titania PS coatings



- $Ti^{(4-\delta)+}$ **valence reduction** in both **μAT** & **nATCZ** PS coatings similar to (but less in magnitude than) Ce

Ti- local structure in PS coatings

- not ana-TiO_2



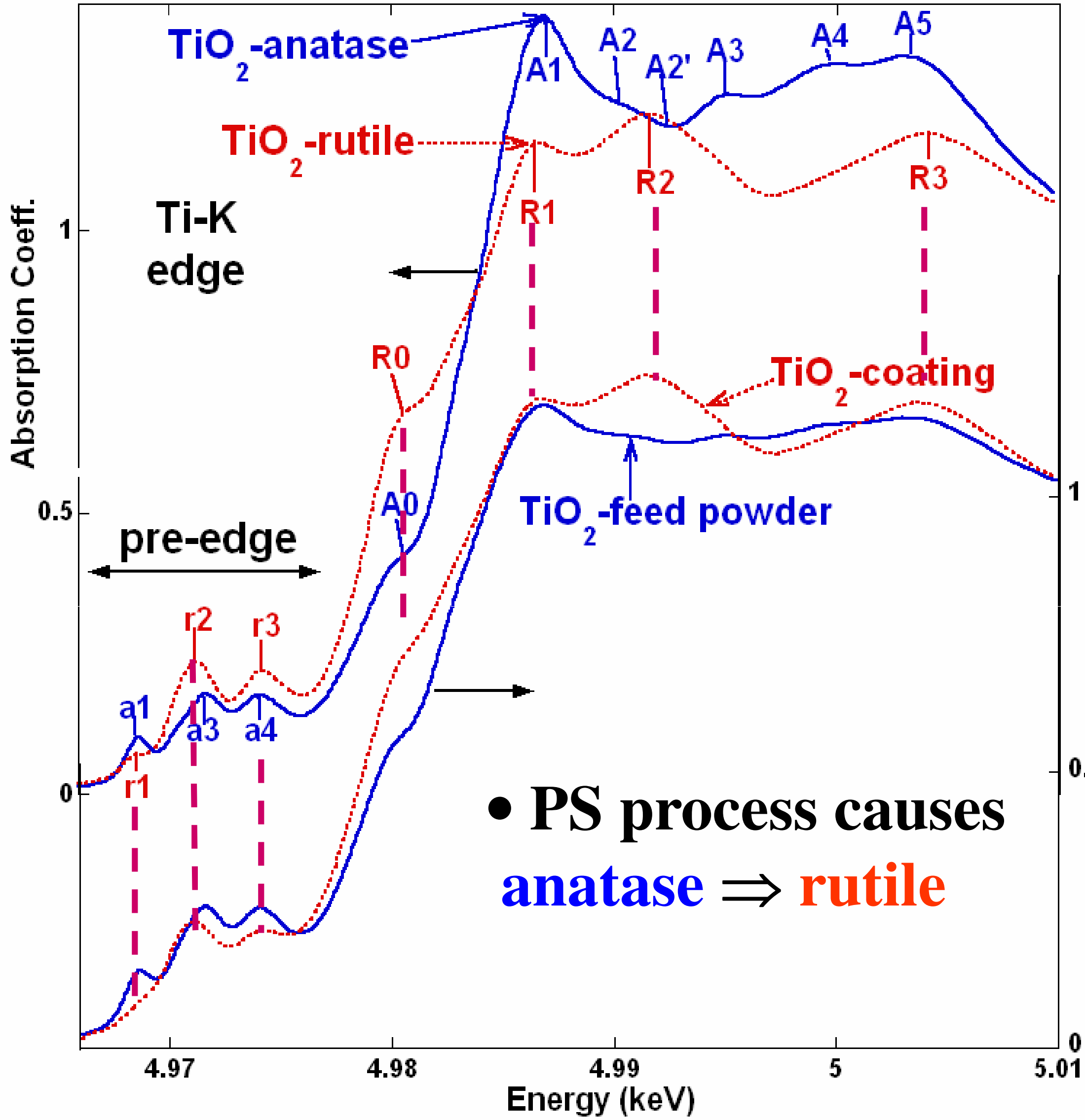
- conjecture** Ti in isolated octahedral sites in spinel γ-Al_2O_3

** U.-Conn. Group electron microscopy: Ti in γ-Al_2O_3

Goberman, Sohn, Shaw,Jordan, Gell. Acta Mat. 2002;50:1141.

Bansal et. al. Acta Mat. 51 (2003) 2959–2970:

Plasma Spray TiO_2 coating (structure) on Ti-6-4



Ti-K edges:
anatase & rutile TiO_2

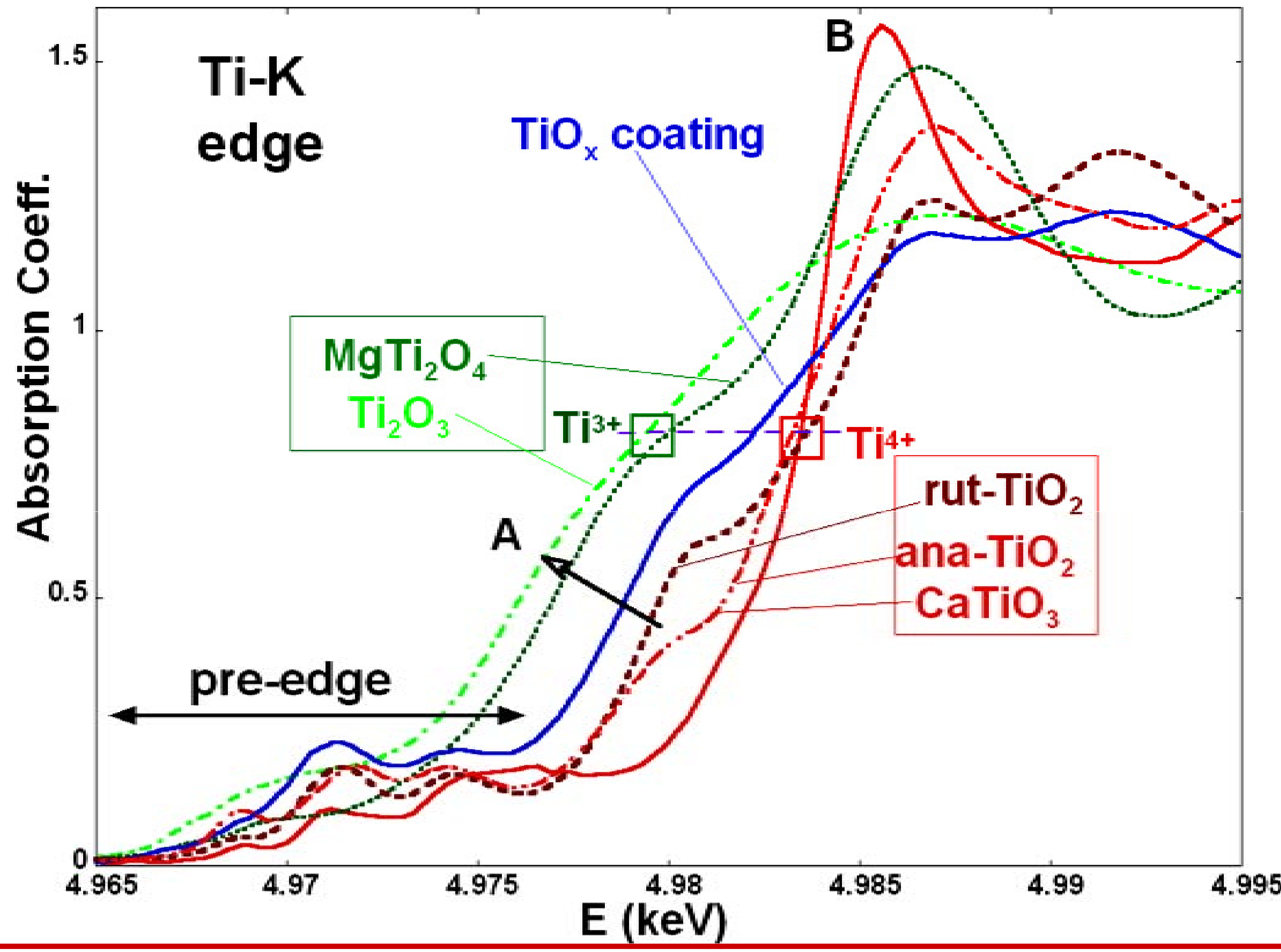
Ti-K edges: TiO_2 feed powder & plasma sprayed TiO_x coating

- **Feed powder**
  dominantly anatase
  (broadened/disordered)

- **PS coating**
  dominant component rutile
  (broadened/disordered)

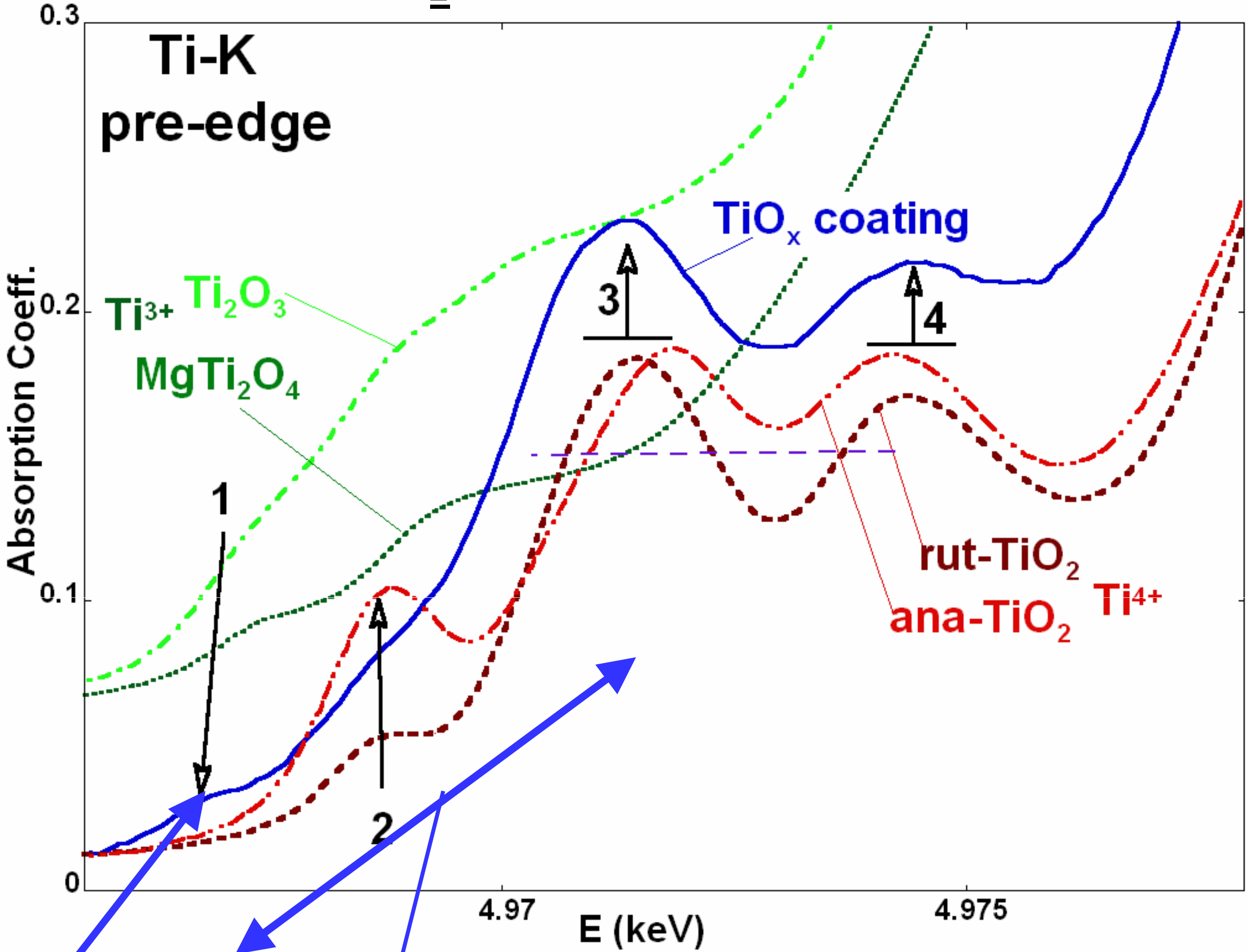
anatase-TiO_2 feed powder ⇒ rutile TiO_x coating

Ti-valence state in TiO_2 PS coatings



- large $Ti^{(4-\delta)+}$ **valence reduction** in PS TiO_x coating
  (δ larger than in aluminia-titania PS coating)

Ti-valence state in TiO_2 PS coatings (pre-edge)



- excess (broad) spectral intensity over Ti^{3+} range
- new spectral feature onset at intensity over Ti^{3+} onset range

- large $Ti^{(4-\delta)+}$ valence reduction in PS TiO_x coating

Summary XAS results on plasma spray coatings

feed powder $\xrightarrow{PS}$ real life coating

local structure
local electronic states/chem

Plasma Spray (PS) Coatings

Al_2O_3-TiO_2: additives; CeO_2, ZrO_2

cubic $Ce^{4+}O_2 \xrightarrow{PS} Ce^{3+}$-O

anatase$Ti^{4+}O_2 \xrightarrow{PS} Ti^{(4-\delta)+}$-O

Chemically reducing PS environment !

cubic $ZrO_2 \xrightarrow{PS}$ octahedral Zr-O

TiO_2

anatase-$TiO_2 \xrightarrow{PS}$ rutile-TiO_x coating

$Ti^{4+}O_2 \xrightarrow{PS} Ti^{(4-\delta)+}O_x$ coating (δ large)

Chemically reducing PS environment !

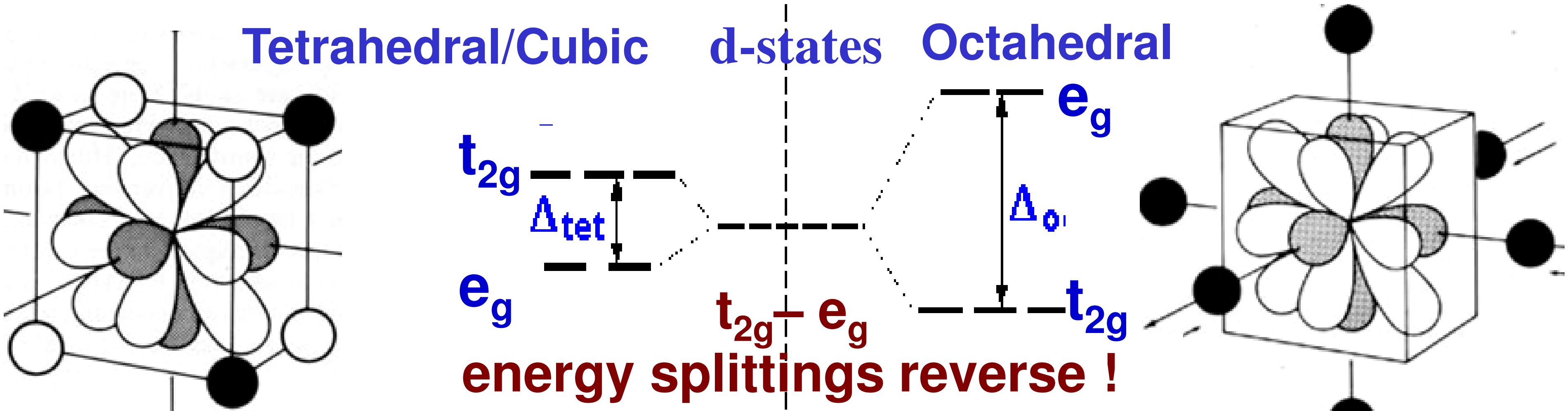
Rutgers Faraday Christmas Children's Lecture

Dec. 2009 **(12th Anniversary)**

(for Children between the ages of 5 and 110 yrs)

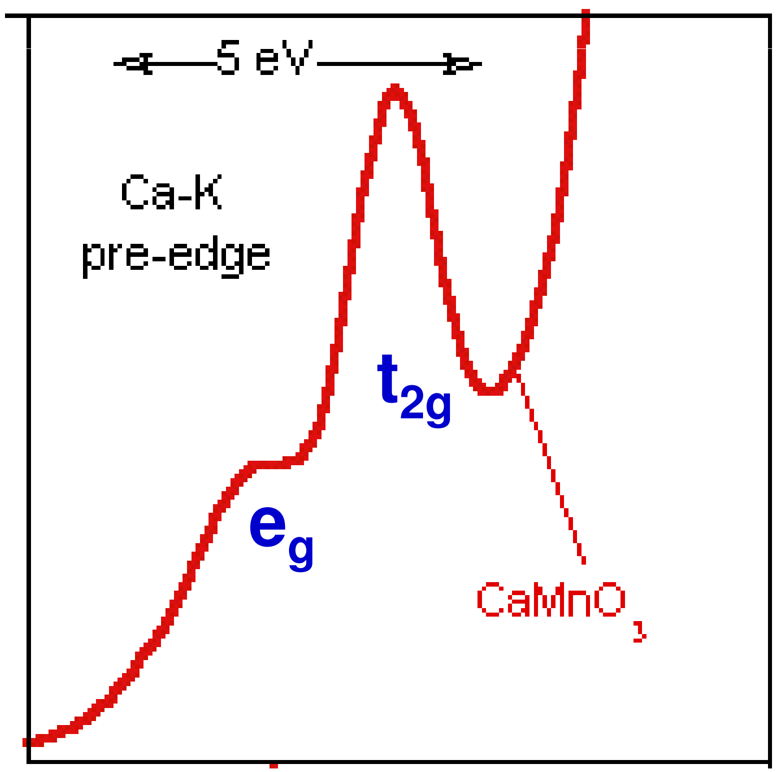
croft@physics.rutgers.edu

web page http://www.physics.rutgers.edu/~croft/FARADAY.HTML



pre-edge: 3d electronic states

Cubic Ca-environment



Octahedral Sc-environment